

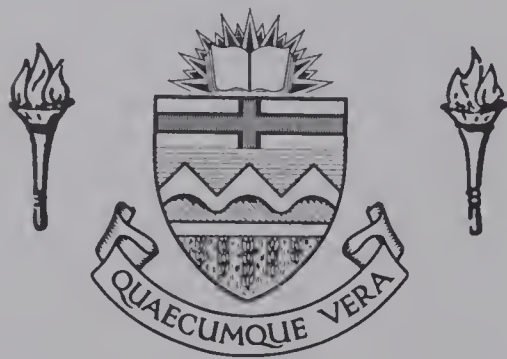
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SOME ASPECTS OF EQUILIBRIUM SOLUTIONS
FOR A SOLONETZIC AND A CHERNOZEMIC SOIL

by

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "Some Aspects of Equilibrium Solutions for a Solonetzic and a Chernozemic Soil", submitted by Shahamat Ullah Khan, B.Sc., M.Sc., (Chem.), M.Sc., (Soil Sci.), in partial fulfilment of the requirements for a degree of Doctor of Philosophy.

ABSTRACT

Sulfate in soil water extracts can be determined accurately by an electrometric method. It involves the precipitation of sulfate by lead nitrate, and the subsequent determination of excess lead ions polarographically. The technique will have a limitation if soil water extracts contain appreciable amounts of organic matter or if chloride concentration is very high ($>56.4 \text{ mmol./l}$).

During periods when the ground water table approaches the surface of the Duagh silt loam soil, the retention of sulfate will be greater in the surface soil than at lower depths. The data indicate that sulfate tends to move more slowly than water in soil.

An abundance of salts in the Duagh silt loam distinguishes it chemically from the geographically associated Malmo silt loam soil. Sodium sulfate is the principal soluble salt present in the former soil. Increasing sodium levels in the Duagh silt loam surface soil were detrimental to barley yield. Nitrogen applied in the ammonium sulfate form was more beneficial for barley growth than applied as sodium nitrate.

Equilibrium ion concentrations and ratios for Duagh silt loam and Malmo silt loam soils at various moisture contents were established by interpolation of ion concentrations in solutions before and after equilibration. Over the moisture range studied, the ionic strengths, electrical conductivities and osmotic pressures of the equilibrium solutions for the different horizons of the Duagh silt loam profile were considerably greater than those for Malmo silt loam. The solubility

of gypsum in the equilibrium solutions of the sub-surface horizons of the Duagh silt loam soil cannot be calculated by the solubility product alone. The association of sulfate ions with cations to form undissociated complex ion-pairs is postulated. The two profiles, also differ markedly with respect to different cation ratios in their equilibrium solutions. The values of ratios for the ion-pairs $K-(Ca + Mg)$, $K-Na$, $Ca-Na$, $Mg-Na$ and $Na-(Ca + Mg)$ were quite different for the two soils. In general, most of the ion ratios varied more markedly with change in moisture for the Duagh silt loam as compared to Malmo silt loam. Variation of sulfate concentration in equilibrium solutions appears to alter significantly certain cation ratios. Over the field moisture range the 'Ratio Law' was applicable for most of the ion-pairs in Malmo silt loam soil and Duagh silt loam surface soil but failed to apply for the sub-surface horizons of the latter soil. The data suggest that sodium adsorption ratio, exchangeable sodium ratio and exchangeable sodium percentage values increased with decrease of moisture in the Duagh silt loam soil.

Solutions of high ionic strength simulating the Duagh soil delayed germination and depressed the yield of barley. High $\frac{Na}{K}$ and $\frac{Mg}{Ca}$ ratios in solutions, particularly the former, increased nitrogen uptake by plants considerably.

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Chapter 1

INTRODUCTION AND OBJECTIVES

There are extensive areas of solonetzic soils in Western Canada and almost all are in the semi-arid and sub-humid grassland and parkland regions. The most common salts in these regions are the sulfates of sodium, magnesium, calcium and potassium; carbonates, bicarbonates and chlorides may also be present in small amounts. The notably high concentration of salts in these soils hinders agricultural production or even makes it impossible when they occur in areas of otherwise fertile soils.

In 1956, the Government of Canada established an Experimental Sub-station at Vegreville, Alberta to study problems related to the productivity of solonetzic soils, particularly under dry land agriculture. The productivity of the soils at the Sub-station varies considerably; the black solonetz (Duagh silt loam) has been the least productive and the geographically-associated eluviated black chernozem (Malmo silt loam) the most productive. In general salinity and/or alkalinity are the most pronounced in Duagh silt loam and least in Malmo silt loam soil. In the field, plants grown on solonetz soils often develop a yellowing of the leaf, while those grown on contiguous chernozem soils do not. This yellowing starts at the tips of the older leaves and eventually the entire plant may die. The condition often becomes progressively worse with successive crops.

For agricultural purposes solonetz soils are regarded as a class of problem soils that require special remedial measures. Considerable research is now being done in relation to the agricultural use of these soils. Such things as deep ploughing to incorporate gypsum and carbonate from lower horizons, the application of manure, gypsum and sulfur and the destruction of the compact B horizon have all received attention. Studies have also been conducted to explore the nitrogen and moisture status in these soils as related to the productivity.

For many years soil scientists have attached considerable significance to the composition and concentration of soluble salts in the soil as being important factors affecting soil productivity. Determining soil solution composition at field moisture contents evaluates the environment of the growing roots. Ideally, the determination of soluble ions should be made on extracts at moisture contents in the field moisture range. However, the preparation of such extracts is time consuming and may require special extraction equipment. A widely accepted method is the saturation extract procedure, and criteria for salinity status and crop tolerances to salinity are often based on the concentration of salts in saturation extracts. However, it is realised that the concentrations of various ions in a soil solution generally do not vary proportionately with change in moisture content of the soil. The total dissolved quantities of some ions increase on change in moisture of soil, while concurrently those of other ions may decrease. The complexity of these changes are further intensified in soils of arid regions because of the greater abundance of soluble salts, the

occurrence of slightly soluble salts and the change in solubility of some salts at high salinities and/or alkalinities. It would thus appear that measurement of salt concentration in saturation extracts might be of limited value for evaluating the productivity of these soils.

The literature suggests that cation adsorption by plants is related to concentration ratios in the solution and it has been established that the ratio of the molar concentration of monovalent cation to the square root of the molar concentration of divalent cation is the important criterion by which to characterize the soil solution. It appears, therefore, that the cation ratio concept has advantages and is less ambiguous than most other approaches. Since no fundamental work of this nature has been done on solonetzic soils, it was thought that an investigation of several cation ratios for a solonetzic and a geographically associated chernozemic soil, over the moisture range normally encountered under the field conditions might assist in establishing some suitable ratios for improving the productivity of the former soil. The author's approach was an attempt firstly, to develop a method for determining the true equilibrium solutions of soils adjusted to various moisture contents and secondly, to study various cation ratios in equilibrium solutions and other properties of the Duagh silt loam and the Malmo silt loam soils. Closely allied to these objectives was an attempt to study the effects of certain cation ratios and ionic strengths of solutions on barley yield and nitrogen uptake.

The problem of accumulation of soluble salts at or near the soil surface in the solonetzic soil under study was also included in this

investigation as it might have an important bearing on equilibrium cation ratios at various moisture contents. When water moves upward to the surface by capillary rise from a permanently or temporarily perched ground water table, it can carry salts with it, mainly sodium sulfate, the principal soluble salt present in the solonetzic soil under study. In many soils, due to ion adsorption, the rate of salt movement may become exceedingly slow relative to the rate of water movement. It is known that sulfate is retained by some soils and this affects its distribution in the profile. For the soil under study, if the upward movement of ground water results in accumulation of soluble sulfate then probably sodium concentration would be correspondingly increased, thereby affecting the cation ratios. It is, therefore, of interest to study the sulfate distribution in solonetzic soil as influenced by water table. Finally, substantial evidence indicates that inspite of the variety of methods available for water soluble sulfate determination in soils, no procedure is completely satisfactory, nor has any one been accepted widely by soil scientists. Since sulfate is the principal soluble anion in the solonetz soil under study, an investigation of its concentration in the equilibrium soil solution as related to several cation ratios was felt warranted. It seemed logical, therefore, that development of an accurate method for determining water extractable sulfate in soils should also be included in this study.

With the foregoing thoughts in mind a study was formulated and the research carried out can be grouped under the following three topics:

- (i) Determination of water extractable sulfate in soils.
- (ii) Sulfate distribution in a solonetzic soil with high water table.
- (iii) Studies on equilibrium cation ratios and other properties of soils.

Each of the above topics is presented as a separate chapter of the thesis, followed by a final chapter summarizing the whole investigation.

Chapter 2

DETERMINATION OF WATER EXTRACTABLE SULFATE IN SOILS

Review of Literature:

The main salts present in the solonetz soils of Western Canada are sulfate of sodium, calcium and magnesium (Bowser, 1961). Accurate estimation of sulfate is essential for characterising such soils. Also, studies relating to the availability of soil sulfur for plant growth are dependent on an accurate method for the determination of small amounts of sulfate. The gravimetric method employed for estimation of sulfate is fairly laborious and time consuming. It involves the precipitation of sulfate in water extracts by BaCl_2 , filtering off, washing, igniting and then weighing the BaSO_4 . The principal source of error involved in this method is co-precipitation. The widespread turbidimetric method suggested by Chesnin and Yien (1950) involves sulfate extraction from the soil with Morgan's solution and the precipitation of sulfate with 30-60 mesh BaCl_2 crystals. The precipitates are kept in suspension with a gum acacia solution, and turbidity readings are made in a photoelectric colorimeter. The turbidimetric method has generally resulted in low values for surface soils and difficulties have been encountered with colored extracts (Hesse, 1957). Also conditions under which turbidity is developed must be controlled closely if reproducible BaSO_4 suspensions are to be achieved. Bartlett and Neller (1960) have determined sulfate by a modified turbidimetric method in soil extracts obtained by Morgan's solution, but it was not satisfactory for all soils studied. The reduction method (Johnson and Nishita, 1952) seems to meet

the requirement of speed and accuracy, but has the limitation of not being specific for sulfate. The modification of this method described by Freney (1958) is lengthy and involves removal of soil colloidal material. It is also necessary to separate sulfate from other inorganic sulfur compounds before this modified reduction method can be used for the estimation of sulfate in soil water extracts. The volumetric methods for the determination of water soluble sulfate based on the use of disodium EDTA (Asghar et al, 1957), B trilon (Myakina, 1960) and thymolphthalein indicator (Puri and Asghar, 1938) are lengthy and subject to some degree of experimental error. The latter has also the disadvantage of calcium salts interference. The colorimetric method for determining water soluble sulfate (Bertolacini and Berney, 1957) is also lengthy and involves the removal of interfering cations with ion exchange resins.

It would thus appear that in spite of the variety of methods available, no one procedure has been widely accepted by soil scientists. It was therefore felt that the first phase of investigation should be concerned with the development of a rapid and accurate method for determining water extractable sulfate in soils. This chapter describes details of such a method developed in this laboratory; it was used for sulfate determination in subsequent studies.

Basic Principle Underlying the Technique:

Lead ions are reduced at a dropping mercury electrode in many base electrolytes giving a well defined polarographic wave and they form a slightly soluble precipitate with sulfate ions. The technique described in this chapter is based on precipitating sulfate in soil extracts with

lead and determining excess of lead ion polarographically using a dropping mercury electrode polarized at a potential corresponding to the diffusion current of lead ions. If the polarograph is set at a particular applied voltage on the diffusion current plateau of the electrolysis wave of lead, the current will be proportional to the concentration of diffusing lead ions in the bulk of the solution. The amount of lead precipitated will be equivalent to the amount of sulfate in the soil extracts.

Materials and Methods:

Soils of a wide range of pH and organic matter content were used in this study (Table 1). The samples were air dried and ground to pass through a 2 millimeter sieve. Organic matter and pH of the saturated paste were determined as outlined by U.S. Salinity Laboratory Staff (1954). Saturation extracts for all soil samples were obtained (Table 1) in addition to a soil-hot water extract (1 : 2) for the chernozemic Ap horizon. Pressure filtration funnels* fitted with Metrical filters were used for obtaining soil water extracts free of clay colloids. Sulfate determinations were made on these extracts.

Preliminary experiments were conducted on a Leeds and Northrup Electrochemograph for the selection of a suitable base electrolyte and proper concentration of gelatin used as maxima suppressor. Since the presence of indifferent salts may cause an increase in the solubility of lead sulfate and also may enhance supersaturation, an ethanol solvent was also used. All solutions were de-aerated with nitrogen. The sulfate in

* Gelman Instrument Company, Ann Arbor, Michigan, U.S.A.

soil extracts was precipitated with an excess of lead nitrate and polarograms were obtained for the free lead ions remaining in solution. Several base electrolytes were tried including 0.1M potassium nitrate, 0.1M potassium chloride, 0.1M nitric acid, 0.1M hydrochloric acid and acidic tartrate (0.4M sodium tartrate + 0.1M sodium hydrogen tartrate). It was found that 0.1M nitric acid gave the most satisfactory results. At constant temperature (25°C.) and drop time (1 drop/4 sec.) reproducible electrolysis waves with half-wave potentials ($E_{\frac{1}{2}}$) of -0.41V vs saturated calomel electrode (S.C.E.) were obtained in 20 per cent ethanol medium containing 0.1M nitric acid as a base electrolyte and 0.005 per cent gelatin concentration. The current attained a limiting value at -0.55V vs S.C.E. and a second electrolysis wave, that marks the reduction of base electrolyte, begins when the dropping mercury electrode becomes more negative than -1.25V vs S.C.E. A typical polarogram obtained in this study is shown in Fig. 1. The foregoing information thus obtained was used in the technique described here.

A simplified inexpensive manual polarograph was assembled (Kolthoff and Lingane, 1952) and a mercury half cell described by Harris (1959) was used to supply a constant potential of -0.85V vs S.C.E. to the dropping mercury electrode. This potential was selected as it lies about half-way on the limiting current plateau of the electrolysis waves obtained in the preliminary studies (Fig. 1). The basic apparatus used is pictured schematically in Fig. 2.

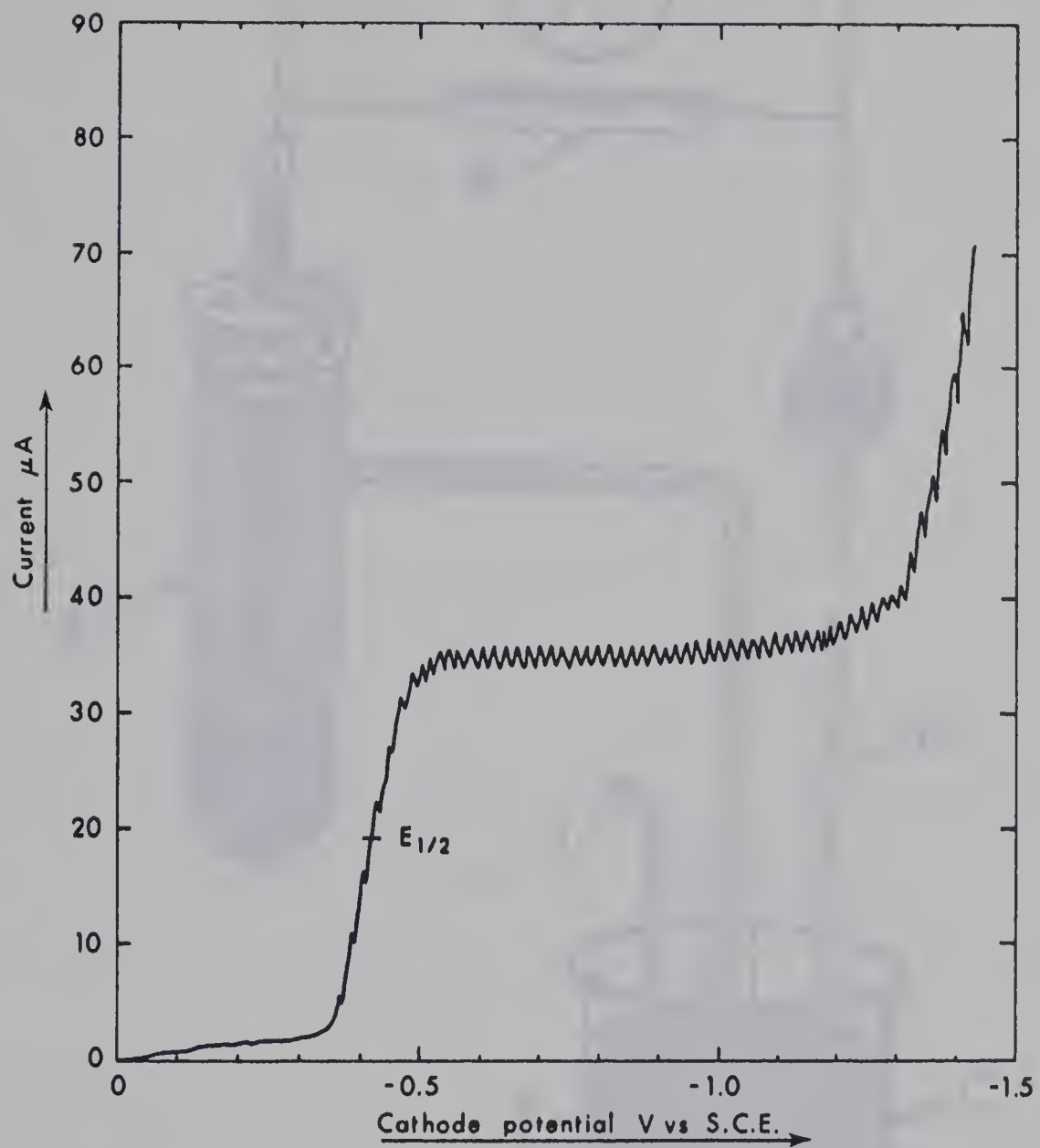


Fig. 1. Polarogram obtained for lead ions after precipitating sulfate in soil extracts

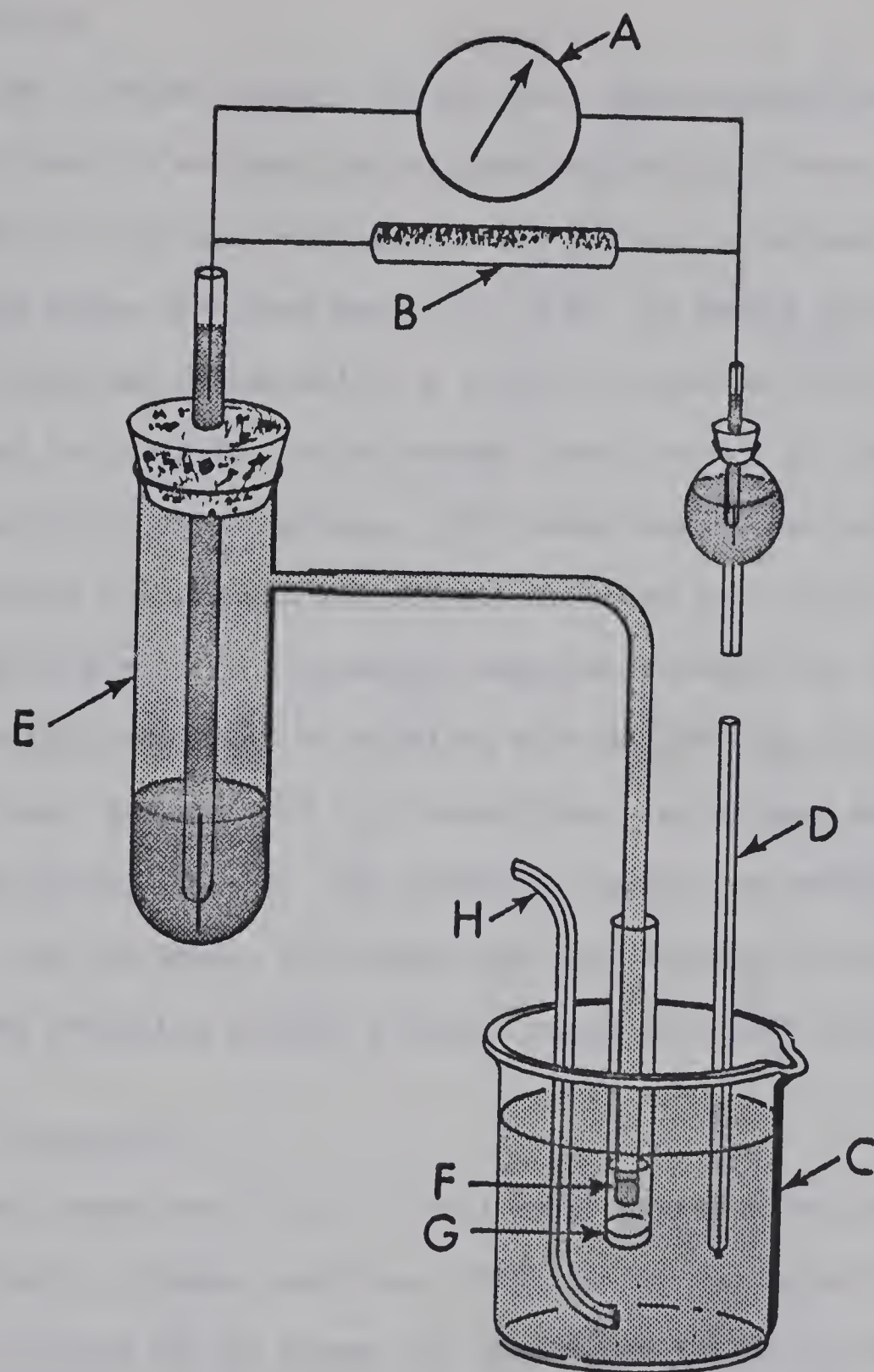


Fig. 2. Diagram indicating simplified polarograph assembled for the determination of sulfate by proposed method

- A - Microammeter, 60 microamperes
- B - Electrolytic condenser, 500 microfarad (for reducing fluctuation in the current)
- C - Electrolytic cell, 50 ml beaker
- D - Dropping mercury electrode
- E - Mercury half cell, -0.85 V vs S.C.E.
- F - Porous glass, 10 mm long and 6.25 mm diameter (Corning, catalogue No. 749303-7930)
- G - Sintered glass
- H - Capillary tube for bubbling nitrogen

The following procedure was adopted for determining sulfate in soil extracts:

Into a 50 ml. beaker, 5.0 ml. soil water extract (more if very low, less if high in sulfate) was transferred and to it were added 2.5 ml. 1M HNO_3 , 0.5 ml. 0.25 per cent gelatin and 5.0 ml. of ethanol. The total volume in the beaker was then made to 21.0 ml. by adding distilled water and the solution was shaken well. A 4.0 ml. aliquot of 0.05M $(\text{Pb}(\text{NO}_3)_2$ was added and the solution in the beaker (total volume 25.0 ml.) was again shaken for about one minute. The beaker was covered with parafilm paper to prevent evaporation and allowed to stand for a half hour. The beaker was then placed in a constant temperature water bath (25°C.) and the solution was de-aerated by bubbling nitrogen through for five minutes. The mercury pool was adjusted to 1 drop/4 sec. and voltage was applied across the electrode system. The diffusion current was measured with a microammeter and the amount of sulfate was read from the standard curve prepared from potassium sulfate solution using the above procedure (Fig. 3).

Results and Discussion:

For comparison, $\text{SO}_4\text{-S}$ in soil water extracts was determined both turbidimetrically (Chesnin and Yien, 1950) and by the method described. The values obtained by the former are lower than those by the new procedure (Table 1). As a means of testing the accuracy of the method, a number of determinations were made on the recovery of potassium sulfate added to soil extracts. Recoveries from soils low in organic matter, with one exception, ranged from 92 to 102 per cent (Table 2). Recoveries were rather low for soils high in organic matter particularly when 5.0 mmol./l of sulfate were added to the extracts (Table 3). This is attributed to the retention of sulfate by organic matter (Freney, 1958; Chao et al, 1962c).

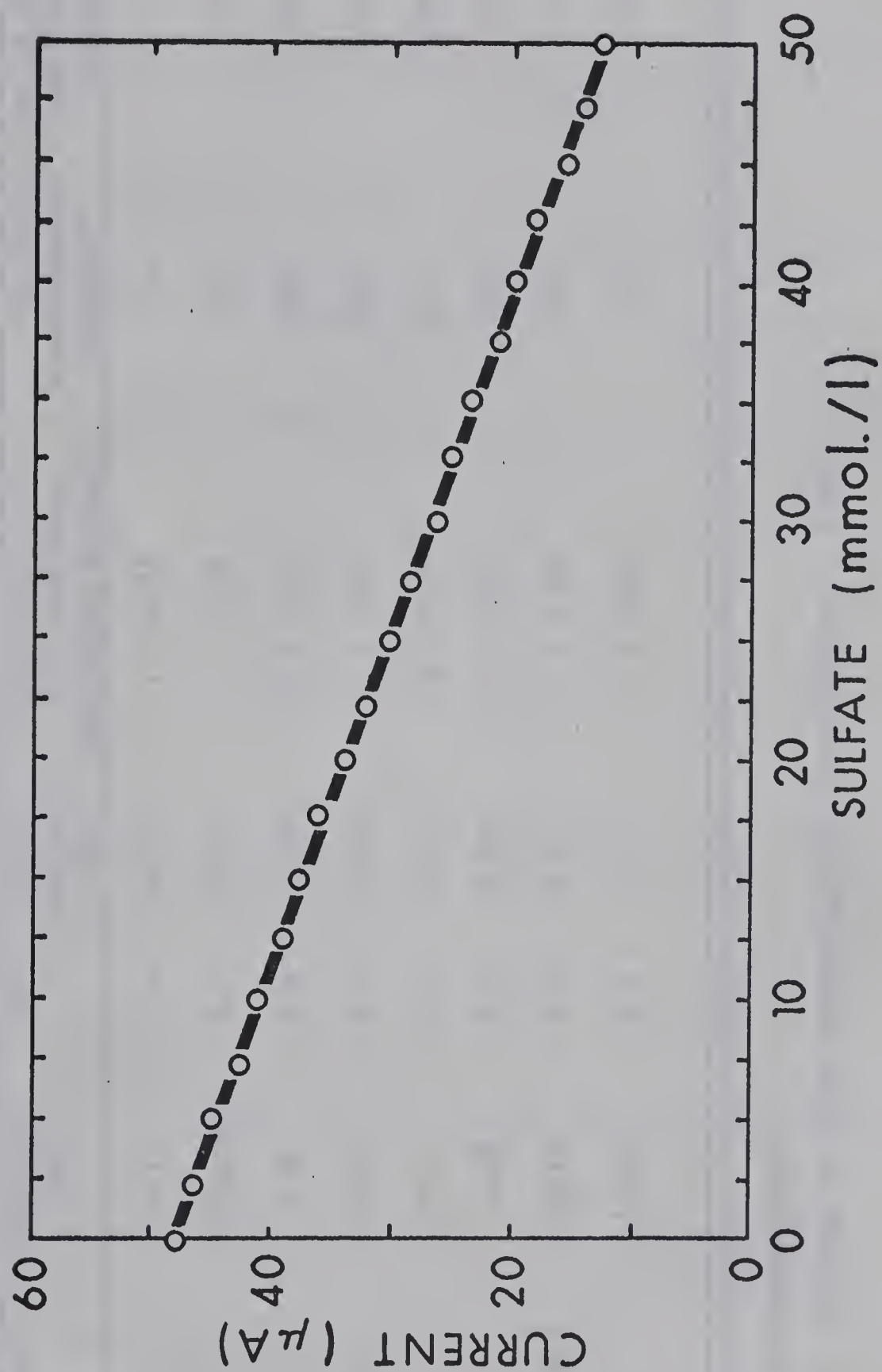


Fig. 3. Calibration curve for sulfate determination by proposed method

TABLE 1

Organic Matter, pH and Water Extractable SO₄-S in Soils Used

Soils	Horizon	Thickness (in)	pH*	Organic matter* (%)	Soil-water ratio for obtaining saturation extracts	SO ₄ -S*** (ppm in soil)	
						Electrometric method**	Turbidimetric method*
Podzol	Bf	6-11	5.9	0.62	1 : 0.55	6	5
Grey wooded	Bt	9 $\frac{1}{2}$ -21 $\frac{1}{2}$	4.7	0.91	1 : 0.75	18	13
Solonetz	Ap	0-4	5.8	9.56	1 : 0.75	320	289
Solonetz	Csa	15-23	8.2	0.88	1 : 0.90	2303	2212
Solonetz	C	23+	8.2	0.87	1 : 0.79	2274	2226
Chernozem	Ap	0-4 $\frac{1}{2}$	5.9	14.98	1 : 0.72	30	23
Chernozem	Ah & Ahe	4 $\frac{1}{2}$ -12	5.9	6.64	1 : 0.65	25	17
Chernozem	Bt ₁	12-26	6.9	1.69	1 : 0.95	37	32

* Average of two determinations

** Proposed method. Average of three determinations (variability \pm 1.8%)

*** Oven-dry basis

TABLE 2

Recovery of Sulfate Added as Potassium Sulfate to Water Extracts
from Soils Low in Organic Matter Using the Proposed
Method (Average of Three Determinations)

Soil	Sulfate in soil extracts (mmol./l)	Sulfate added (mmol./l)	Total sulfate measured (mmol./l)	Recovery (%)
Podzol (Bt)	0.36	5.0	5.36	100
	"	15.0	15.7	102
	"	25.0	24.6	97
Grey Wooded (Bt)	0.75	5.0	4.95	84
	"	15.0	14.9	95
	"	25.0	24.4	95
Solonetz (Cca)	20.0	5.0	24.7	94
	"	15.0	34.4	96
	"	25.0	44.4	97
Solonetz (C)	22.5	5.0	27.2	94
	"	15.0	37.4	100
	"	25.0	46.3	95
Chernozem (Bt ₁)	1.20	5.0	5.80	92
	"	15.0	16.2	100
	"	25.0	26.0	99

TABLE 3

Recovery of Sulfate Added as Potassium Sulfate to Water Extracts
from Soils High in Organic Matter Using the Proposed
Method (Average of Three Determinations)

Soil	Sulfate in soil extracts (mmol./l)	Sulfate added (mmol./l)	Total sulfate measured (mmol./l)	Recovery (%)
Solonetz (Ap)	13.3	5.0	17.8	90
	"	15.0	27.4	94
	"	25.0	38.3	100
Chernozem (Ap)	1.30	5.0	3.49	44
	"	15.0	14.7	89
	"	25.0	25.6	97
Chernozem (Ap) (Hot water extract)	0.95	5.0	3.44	50
	"	15.0	14.1	87
	"	25.0	23.9	92
Chernozem (Ah & Ahe)	1.20	5.0	4.08	58
	"	15.0	13.1	79
	"	25.0	24.3	93

Further experiments were carried out to study the possible interference of organic matter in soil extracts on sulfate determination. The results reported in Table 4 were obtained by following two procedures. Sulfate was determined in soil water extracts (column 2) and then potassium sulfate was added to the extracts. Organic matter in these extracts was oxidized by treatment with 30 per cent H_2O_2 . The treatment consisted of adding 1 ml. aliquot of H_2O_2 each time followed by digestion on a hot water bath until the extracts become colorless and reaction subsided substantially. In these oxidized extracts sulfate was determined (column 4) and recoveries calculated (column 5). In a second procedure the soil water extracts were treated with 30 per cent H_2O_2 and digested on a hot water bath and sulfate determined (column 6). To these oxidized extracts potassium sulfate was added and total sulfate determined (column 8). The recoveries thus calculated are shown in the last column of Table 4. It would appear that the recoveries were higher in the range of 1.0 to 7.0 per cent (column 5, Table 4) obtained by the first procedure as compared to the second (column 9, Table 4). This suggests the oxidation of water extractable organic sulfur to inorganic sulfate and the release of organic matter bound sulfate. The results are in agreement with those of Williams and Steinbergs (1959). Consequently if the extracts are oxidized it is important to realize that the organic sulfur extracted will be oxidized to inorganic sulfate in addition to release of organic matter bound sulfate. The data shown in Table 4 appear to lend support to this conclusion. The fact that per cent recoveries were higher when sulfate was added to oxidized extracts (column 9, Table 4) than before

TABLE 4

Effect of Organic Matter on the Recovery of Added Sulfate
(Average of Three Determinations)

Soil	Sulfate in soil extracts (mmol./l)	Sulfate added (mmol./l)	Total sulfate measured after treatment with H ₂ O ₂ (mmol./l)	Recovery (%)	Sulfate in soil extracts after treatment with H ₂ O ₂ (mmol./l)	Sulfate added (mmol./l)	Total sulfate measured (mmol./l)	Recovery (%)
Solonetz (Ap)	13.3	5.0	18.6	106	13.7	5.0	18.6	99
	"	15.0	28.2	99	"	15.0	28.0	95
	"	25.0	39.2	104	"	25.0	38.7	100
Chernozem (Ap)	1.30	5.0	5.05	75	1.54	5.0	5.09	71
	"	15.0	15.3	93	"	15.0	15.4	92
	"	25.0	26.8	102	"	25.0	26.8	101
Chernozem (Ap) (Hot water extracts)	0.95	5.0	5.80	97	1.34	5.0	6.03	94
	"	15.0	16.7	105	"	15.0	16.6	102
	"	25.0	27.2	105	"	25.0	27.1	103
Chernozem (Ah & Ahe)	1.20	5.0	6.45	105	1.32	5.0	6.42	102
	"	15.0	15.4	95	"	15.0	15.5	94
	"	25.0	27.0	103	"	25.0	26.8	102

organic matter removal (column 5, Table 3) clearly illustrates the interference of organic matter in accordance with the earlier findings (Freney, 1958; Chao et al, 1962c). This investigation did not determine the nature of organic matter bound sulfate in the soil extracts. Treatment with H_2O_2 prior to sulfate determination by this method had no effect on the electrolysis wave of lead.

In order to get an indication of the possible effect of chloride on sulfate determination by this technique, a number of determinations were made on the recovery of added sulfate to the soil (solonetz Csa) water extracts containing added chloride in the form of KCl. Results of these tests are reported in Table 5. It would appear that up to the chloride ion concentration of 56.4 mmol./l the recoveries of added sulfate were within the range of 95 to 98 per cent. However, with a further increase the per cent recoveries of added sulfate decreased gradually, thereby indicating an increase in the solubility of lead sulfate. This effect has also been reported elsewhere (Kolthoff and Yu-Djai, 1940; Zhdanov and Yakovlev, 1958). The data suggest lead was not precipitated by chloride ions under the experimental conditions described. However, this technique will have a limitation if the concentration of chloride ions in soil water extracts is exceptionally high. Other ions normally found in soil water extracts will not interfere.

Under the proposed experimental conditions this method will determine accurately as little as 80 μg SO_4-S in the measuring vessel. However, for soils very low in SO_4-S the water extracts may be concentrated by evaporating on a gently boiling water bath. Some organic sulfur may be released by heating water extracts of soils high in organic matter thereby

TABLE 5

Effect of Chloride Concentration on the Recovery of Added Sulfate in
Solonetz Csa Soil Extract (Average of Three Determinations)

Chloride concentration in soil extract (mmol./l)	Recovery (%)	Chloride concentration in soil extract (mmol./l)	Recovery (%)
0.4	97	39.5	95
2.3	96	45.1	98
5.6	98	50.8	96
8.5	96	56.4	94
11.3	98	62.0	91
14.1	96	67.7	88
16.9	96	73.3	84
19.7	95	79.0	83
22.6	96	84.6	80
25.4	96	98.7	76
28.2	96	112.8	72
33.8	95		

resulting in higher values (Williams and Steinbergs, 1959). In such cases, this technique will have a limitation. Another approach would be to use a commercial polarograph having greater sensitivity. The capacity of the half cell used is sufficient to allow many hundreds of analyses to be made without measurable change of potentials (Harris, 1959). Since the influence of temperature and drop time on the diffusion current is quite marked (Kolthoff and Lingane, 1952) it is recommended that the temperature of the solutions be controlled to $\pm 0.5^{\circ}$ C. or better, and mercury drop time be adjusted to some value between 3 and 5 seconds. These must be kept constant throughout all analyses. The electrode assembly should be shock mounted for protection from vibration

The proposed technique was primarily developed to fill a need for both an accurate and quick method for determining water soluble sulfate in the soils under study. Notwithstanding this fact, as it would appear from the data of this investigation, this technique can also be adopted successfully for other soils as well. Details of the proposed method and some experimental results of this investigation have also been reported elsewhere (Khan and Webster, 1968).

Chapter 3

SULFATE DISTRIBUTION IN SOLONETZIC SOIL WITH HIGH WATER TABLE

Review of Literature:

Sulfate ions are known to be retained by soils; however the extent of retention depends on various soil conditions. Ensminger (1954) showed that sulfate was retained to a certain extent by most soils. The sub-surface layers of the soils he studied usually contained more sulfate and were capable of adsorbing more sulfate than the surface layers. He also found that surface layers of most of the light textured soils did not contain much sulfate or did not have a capacity to adsorb sulfate from solution. Neller (1959) found much more sulfate in the sub-surface horizons than in the surface layers. These high sulfate levels were found generally where clay was prominent in the profile. Berg and Thomas (1959) showed that sulfate was held much more tightly than chloride in all the soils studied. Kamprath et al (1956) studied some of the factors affecting sulfate adsorption by soils. Their results suggest that the soils which contained a relatively large amount of 1 : 1 type clay minerals adsorbed more sulfate than the soils containing predominantly 2 : 1 type clay minerals. The amount of sulfate adsorbed decreased as the pH of the soil suspension increased from 4 to 6. For all the soils they studied, increasing the phosphate concentration in the solution reduced the amount of sulfate adsorbed by the soil. Results of various other investigations (Chao et al, 1962a; 1962b; Swoboda and Thomas, 1965) suggest that on leaching soil columns sulfate tends to move downwards more slowly than water in weathered soils, because of the retention of

sulfate. The sulfate adsorption under equilibrium conditions as affected by such soil constituents and properties as organic matter, free iron and aluminum oxides, type of clay minerals, and the acid nature of the clays have received considerable attention (Chao et al, 1962a). Also, the mechanism of the processes involved for the reaction and movement of sulfate in soil systems has been discussed in the literature (Harward and Reisenauer, 1966).

Very little information is available on sulfate movement and its distribution in Solonetzic soils. Those in north central Alberta occur in relatively flat, ground water discharge areas where the capillary rise from a permanent or temporarily perched water table is sufficient to maintain a high salt level in the lower B horizons (Arshad and Pawluk, 1966). Sodium sulfate is the principal soluble salt present in these soils. Arshad and Pawluk (1966) reported that in areas where drainage was inhibited, the movement of capillary moisture towards the surface during the periods of low precipitation moved sodium ions upward in larger concentration than either magnesium or calcium ions. From these results it would be suspected that concentration changes of sodium will generally follow those of sulfate. However, further research is needed to substantiate this hypothesis.

It was deemed desirable, therefore, to obtain general information on the pattern of sulfate movement for the solonetz soil under study as influenced by the presence of a water table and, if possible, to associate this information with some soil characteristics or properties. Since sulfate would likely be accompanied by sodium, it was felt that

information from this investigation might be of value in cation ratio studies as their constancy or otherwise may possibly be affected by sulfate distribution in the soil profile as a result of capillary rise from the ground water table. This problem was studied under laboratory conditions with the use of soil columns. The movement of sulfate in the columns containing different soil horizons was followed with the use of S^{35} tagged sodium sulfate. Details of the technique used and results of this study are discussed herein.

Materials and Methods:

Thin Duagh Loam soil from an area near Vegreville, Alberta was used for this study and the following horizons were sampled during the summer of 1963: Ahe, : 0-5", Bnt₁, : 5-11", Bnt_{2sa} : 11-17" and Cca : 17"+. The soil samples were air dried and ground to pass through a 2 millimeter sieve. The mechanical analysis for each soil horizon was conducted, using the method outlined by Toogood and Peters (1953). All other methods were as outlined by U.S. Salinity Laboratory Staff (1954) except for acid soluble phosphate which was extracted with 0.001M H_2SO_4 buffered with $(NH_4)_2SO_4$. The air dried screened soils from the different horizons were uniformly mixed with washed dry sand (1 : 1 by volume) and used for the column study.

Column Study:

Plastic tubing segments, 1.5 inches in diameter, 1 inch and 2 inches in length were connected with wax and then wrapped with electrical tape, first at 1 inch intervals to 18 inches and then at 2 inch intervals to 24 inches. The entire column was then painted with rubber cement to

make it water tight. A 1 inch layer of 20-30 mesh washed sand was spread evenly in the bottom of the columns, burying an inlet tube which lead to a constant level reservoir, the end of the tube in the column being protected with glass wool. The water table was initially adjusted to the surface of the sand layer 1 inch above the base of the column. The column was then filled to the 1 inch level above the surface of the sand layer with Cca horizon material saturated with water. This was achieved by adding a small portion of soil material and water, with the reservoir water inlet running until the required level was reached. The water table was thus maintained at the 2 inch level while filling the columns. This technique was adopted to establish accurately the level of the water table at the beginning of the experiment and also to exclude any air bubbles. A 2.30 ml. aliquot of tagged sodium sulfate solution ($5 \times 10^{-4}M$) containing 1 mc. $S^{35}O_4$ was added uniformly to the surface at this 2 inch level and the remainder of the column was filled with dry soil from different horizons according to the natural sequence found in the field (Fig. 4). As each increment of soil material entered the column, the side of the column was gently tapped to aid in uniform packing and the soil was then tamped gently several times with a rubber stopper fixed on the end of a long glass tube. An attempt was made to systematise the operation of packing so that uniform density within each soil horizon could be expected. The columns were packed in duplicate.

The water level in the reservoir was increased 1 inch every two days until it reached a height of 10 inches above the base of the columns. The columns were then allowed to stand for two weeks when the whole soil

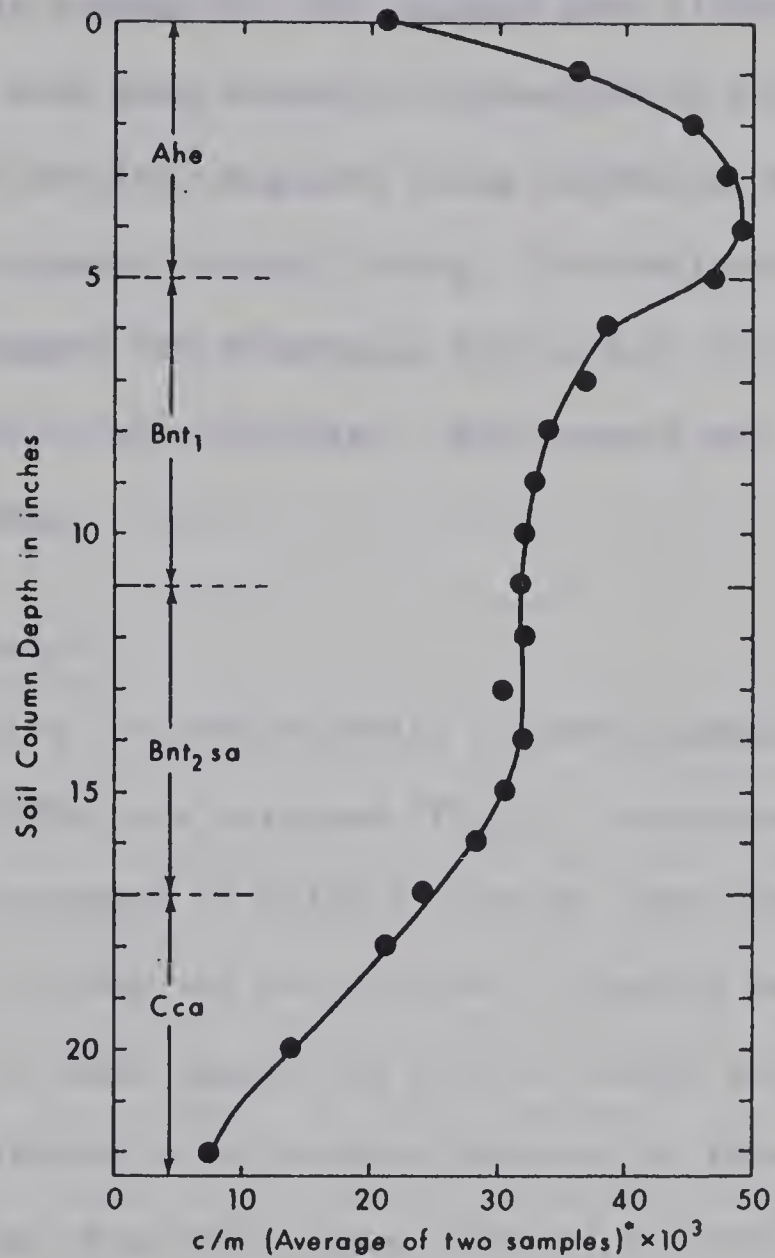


Fig. 4. Distribution of $S^{35}O_4$ in Thin Duagh loam soil

* Variability $\pm 7.9\%$

column had been thoroughly wetted by capillary rise. During this period surface evaporation was reduced by covering the tops of the columns with parafilm paper. As soon as the wetting front reached the surface, the water reservoir was removed and the columns were allowed to drain for three days. They were then carefully dismantled by peeling off the tape and slicing the column into segments being careful to maintain similar geometry for each segment during slicing. The radioactivity of the top surface of each segment was determined with a G.M. thin mica window counter and a tracter-lab autoscaler. Each sample was counted three times and the average taken.

Results and Discussion:

By counting the radioactivity of each segment, the relative concentration of $S^{35}O_4$ thus obtained (Fig. 4) indicates a well-defined pattern of upward movement of sulfate from the water table. Distribution of sulfate in the columns was not uniform; retention was greater near the surface than at lower depths and this is likely partly responsible for accumulation of sulfate in the surface horizons of this soil in the field during periods when water comes close to the surface*. Evaporation would affect the distribution pattern but in this study its influence was negligible because it was maintained at a low level.

It is known that anion exchange increased in soil colloids with increase in acidity thus causing more sulfate retention and, in general, the amounts of sulfate retained above pH 6-7 are not significant

* Personal communication with Dr. R. R. Cairns, Soil Research Sub-station, Vegreville, Alberta.

(Harward and Reisenauer, 1966). Kamprath et al (1956) have found that sulfate retention decreased as pH of the soil suspension increased from 4 to 6. It would appear (Fig. 4, Table 6) that in the lower horizons the sulfate concentration in the column decreased with decreased acidity; however, this relation was not observed for the surface soil as indicated by the wide variation of sulfate retained in the surface five inches with no apparent change in pH. Sulfate could be held by the positive charges of soil organic matter on the basis of its amphoteric properties. Chao et al (1962b) found that soil organic matter increased sulfate adsorption and its removal reduced retention one-third to one-half for each of the two soils used. In this study the data do not bear out this effect entirely. The organic matter content of the 11 - 17 inch layer was less than one-half that in the 5 - 11 inch layer but sulfate distribution was approximately the same. Chao et al (1962a) in their studies found that the movement of S^{35} was negligible in Aiken and Knappa soils although the former contained 6.8 per cent and the latter 18.3 per cent organic matter. On the other hand, the movement in Wingville and Barran soils was much greater than in the Aiken which had approximately the same organic matter content. They are of the opinion that possibly there may have been qualitative differences in the organic matter for the various soils. In this connection the results of the investigation reported in previous chapter are of interest and substantiate Chao et al (1962a) observations. It would appear that sulfate, added to water extracts from Chernozem (Ah & Ahe) was retained to a greater degree than in those from the Solonetz (Ap) horizon (Table 3) even though the former contained

TABLE 6
Some Properties of Thin Duagh Loam Soil Used in S³⁵O₄ Movement Study
(Average of two Determinations)

Horizon	Thickness (in)	pH	Organic matter (%)	Acid soluble P ppm	Clay <2μ (%)
Ahe	0-5	6.1	7.4	42	28
Bnt ₁	5-11	7.4	2.9	47	36
Bnt _{2sa}	11-17	7.8	1.2	47	40
Cca	17-23*	8.4	0.9	82	44

* S³⁵O₄ placed at 22" depth

6.6 per cent and the latter 9.6 per cent organic matter. Kaolin minerals adsorb more sulfate than montmorillonoids; however, this is not always the only factor as many soils which did not show strong retention of sulfate, contained kaolin (Chao et al, 1962a). In the soil used for this study montmorillonite is the major clay mineral (Arshad and Pawluk, 1966b). It appears that an increase in percentage of clay had a diminishing effect on sulfate retention in the lower horizons; however, this effect was not consistent for the upper horizons (Fig. 4, Table 6). In contrast, Neller (1959) reported that for a soil containing a large amount of montmorillonite the upper three horizons showed a decrease in sulfate content with a decrease in clay. The same trend was observed for soils containing mainly kaolinite, gibbsite and illite clays. The sulfate retention in the soil studied was lowest in 17 - 33 inch layer containing the most soluble phosphate. From 5 to 17 inches the phosphate concentration was constant and there was no marked variation in sulfate movement. Kamprath et al (1956) found that increasing the phosphate concentration in the solution reduced the amount of sulfate adsorbed by the soil. From the foregoing it is evident that many factors affect sulfate retention in soils.

In general, the data support the earlier findings (Chao et al, 1962a; 1962b; Swoboda and Thomas, 1965) that sulfate tends to move more slowly than water in soil. When the water front reached the surface the sulfate front was still at the four or five inch layer.

The results of this investigation are valuable, not only in illustrating the pattern of sulfate movement in the soil under study, but also in suggesting the changes in cation concentration which will accompany those of sulfate. Elgabaly and Naguib (1965) concluded that

the depth to ground water contributes more to the salinization of the soil surface than does the salinity level of ground water. However, their results also suggest that the higher chloride and sodium concentrations were in the ground water, the higher were their concentrations in the soil. According to Eremin (1953) salinity is caused by the nearness of the ground water to the soil surface. Furthermore, he found easily soluble chlorides and sulfates near the surface in greater concentration than the carbonates. In view of the foregoing it is logical to assume that greater accumulation of sulfate near the surface as the result of high water table will also result in a corresponding increase of sodium, since sodium sulfate is the principal soluble salt present in the soil under study. This assumption is substantiated by the fact that in Solonetzic soil areas of Alberta where drainage was inhibited, the movement of capillary moisture towards the surface during the periods of low precipitation moved sodium upward in larger concentration than either magnesium or calcium (Arshad and Pawluk, 1966a). This will thus affect cation ratios in equilibrium soil solutions and this aspect of the problem is considered in the next chapter. The investigation described in this chapter has also been reported elsewhere (Khan and Webster, 1968).

Chapter 4

STUDIES ON EQUILIBRIUM CATION RATIOS AND OTHER PROPERTIES OF SOILS

Review of Literature:

The problem of saline and alkali soils is an old one and there is extensive information on this subject in the technical literature. It is not the intention of the author to make this section voluminous by presenting a comprehensive review of literature on these soils; rather it was deemed more desirable to cite only important references whenever necessary. However, for the clarity of the problem under study, a brief review of literature dealing with ion ratios and related subjects was felt warranted.

Early work in soil moisture considered the soil solution as the culture medium in which plant roots were bathed and a great deal of emphasis was placed on appropriate methods for expressing this solution. According to Moss (1963a), the soil-water equilibria are dynamic in nature and plant roots will grow best in the intermicellar soil solution, as least energy would be expended by the plants in obtaining their requirements provided other factors do not become limiting. Schuffelen and Bolt (1958) have emphasized the determination of activity ratio of ions in soil solution and considered it as the best approach in assessing nutrient supply to plants. However, Olsen and Peech (1960) expressed the view that the classical soil-solution composition theory as postulated by Cameron (1911) should completely define the ionic environment of plant roots.

There is as yet no generally recognized view of the mechanism of ion uptake by roots which would allow a definite soil expression to be

identified as the quantity controlling the uptake. However, it is postulated that uptake of cations from a nutrient solution is the same whether an exchangeable phase is present or not (Lagerwerff, 1958; 1960; Olsen and Peech, 1960), and plants grow well in extremely dilute solutions provided that an adequate supply of solution is maintained (Williams, 1962). This suggests that plants take up cations directly from the soil solution, with the large bulk of exchangeable cations acting as a reservoir from which the solution is replenished. Moss (1964a) presents a review of various theories on ion uptake and his and Broeshart's work (cited by Moss) support the view that cation adsorption by plants is related to concentration ratios in the soil solution. Woodruff (1955a; 1955b) has suggested that differences in cationic concentration and differences in cationic ratios in the soil solution are of no fundamental significance, whereas the ratio of the molar concentration of monovalent cation to the square root of the molar concentration of the divalent cation, which reflects the energy of exchange, is the important criterion by which to characterise the soil solution.

In a soil soil-solution system the cations associated with anions in solution are in equilibrium with exchangeable cations held by negative charges on the soil. Diluting the system will result in a change of equilibrium. The effect of dilution on the composition of a soil solution has been investigated by several workers and the subject was extensively reviewed by Parker (1921) and Reitemeier (1946). According to Eaton and Sokoloff (1935) the proportion of divalent to univalent cations is decreased on diluting the soil solutions. Schofield (1947) explained the relationship between adsorbed ions and ions in solution over a

specified concentration range, by a "Ratio Law" which can be expressed as follows:

$$\frac{[M_1]^{\frac{1}{z_1}}}{[M_2]^{\frac{1}{z_2}}} \quad \text{or more strictly} \quad \frac{(M_1)^{\frac{1}{z_1}}}{(M_2)^{\frac{1}{z_2}}} = \text{a constant}$$

Where brackets denote concentrations; parentheses denotes activities and M_1 and M_2 are cations of valency z_1 and z_2 in dilute solutions in equilibrium with adsorbed cations. The law depends upon certain assumptions which Schofield himself had shown in his original paper not to be applicable to all soils. Schofield and Taylor (1955b) have demonstrated the applicability of the law to Rothamsted soils for the ion-pairs H-Na, H-Ca and H-Al and to five Rothamsted soils for the ion-pairs H-(Ca + Mg) (Schofield and Taylor, 1955a). Beckett (1964a) confirmed the ratio law for the ion-pair K-(Ca + Mg) for soils in the Oxford area. However, Taylor (1958) working with the ion-pair K-(Ca + Mg), found that two out of the four Rothamsted soils did not conform to the law. The constancy of several ion-pairs for different soils has been tested by many other workers (Nichol and Turner, 1957; Turner and Nichol, 1958; Salmon, 1964; 1965; Moss, 1963a; 1963b; Moss and Hodnett, 1963). Recently Khasawneh and Adams (1967) concluded that the ratio law was adequate to describe the change in the relative amount of K to Ca upon dilution of one soil system, but a correction term was added to the formulation of the ratio law in order to describe the data of the other soil system. It may be pointed out, however, that the foregoing studies were conducted on non-saline soils and to the author's knowledge similar studies have not been reported for saline and/or alkaline soils.

The use of ion activities rather than concentrations is a fairly recent development in soil chemistry. The concept of ion-activity ratios has been used extensively on the assumption that they influence the uptake of ions by plants. Several recent studies (Taylor, 1958; Moss, 1963a; 1963b; 1963c; Moss and Hodnett, 1963; Moss, 1964a; 1964b; Beckett, 1964a; 1964b; Tinker, 1964a; 1964b; Salmon, 1965; Beckett et al, 1966) have emphasized the importance of ion-activity ratio functions and their possible use in the measurements of potassium status of soils. The activity of ions present in the soil solution phase may be calculated in the same way as for pure solutions. In dilute solutions the individual ion activity coefficient is given by the Debye-Huckel equation.

$$-\log f = \frac{Az^2\sqrt{I}}{1 + a^0 B\sqrt{I}}$$

where z is the valency of the ion concerned and I is the ionic strength of the solution. A and B are constants characteristic of the solvent, at the specified temperature and pressure. Values of these constants for aqueous solutions have been reported in the literature (Manov et al, 1943). The quantity a^0 has a value dependent upon the "effective diameter" of the ion in solution and is determined by experimentation. The values of a^0 for several individual ions in aqueous solutions are reported elsewhere (Klotz, 1950). The physical significance of a^0 , which is commonly related to the diameter of the ion in solution, merits a brief digression. Values of a^0 are ordinarily larger than values of ionic diameters given for ions in crystals. This difference presumably stems from the envelope of water molecules that surround the ion in aqueous

solutions. Wiklander (1964) has suggested consideration of a^0 values in calculation of ion activity coefficient from the above equation. The calculated activity coefficient will in this way include the effect of ion hydration.

The ionic strength I is half the sum of the concentration of each ion in the solution multiplied by its charge squared. Mathematically it can be expressed as:

$$I = \frac{1}{2} \sum C_i z_i^2$$

where C_i is the concentration and z_i is the charge of the i th ion in the solution, the summation being taken over all ions, positive and negative. Ionic strength is a relation useful in comparing solutions of diverse composition because the specific electrical effects of the interactions of the variously charged ions present are taken into consideration. Because electrical effects are a function of the square of the charges on the ions, use of ionic strength gives a more useful criterion of the behaviour of a solution than does concentration. To calculate ionic strength of soil solution, one must determine the major ions present. Undoubtedly traces of several other cations and anions may be present also but their total contribution would be unlikely to change the ionic strength determined appreciably.

"
The Debye-Huckel expression cited previously has been used widely by soil scientists to determine the activity coefficient of ions in solution. However, it is realized that this equation is accurate only at very low concentrations. Beckett (1965) has pointed out that
" the Debye-Huckel limiting law is applicable only up to ionic strengths

of 0.01 M or thereabouts and for soil solutions no more than approximately 0.003 M. The author is, however, aware that some workers (Taylor, 1958; Moss, 1963b) have used the second approximation for solutions of considerably greater ionic strength than the suggested upper limit. For more concentrated solutions various other empirical expressions have been suggested in the literature, but all reduced to the limiting formula of Debye-Huckel at higher dilutions. A good review of several empirical expressions has been presented by Robinson and Stokes (1959). Beckett (1965) considered the Guggenheim equation (Guggenheim, 1935) to be satisfactory for soil solutions upto an ionic strength of 0.03 M. According to Butler (1964), Davies equation (Davies, 1938) is very satisfactory for a reasonable estimate of activity coefficient of ions in solution. Davies equation is essentially a slight modification of the Guggenheim expression and can be represented as follows:

$$- \log f = \frac{Az^2 \sqrt{I}}{1 + \sqrt{I}} - 0.2 Az^2 I$$

The terms used here have been previously defined. At an ionic strength $I = 0.1$ M the error in determining activity coefficient by the above equation will be less than 3 per cent and at $I = 0.5$ M less than 8 per cent (Butler, 1964).

In the opinion of the author, Davies expression appears appropriate for calculating ion activity coefficients in dilute soil solutions provided attention is paid to the ionic diameter a^0 , a point which has been emphasized by Wiklander (1964). Therefore, in this investigation activity coefficients for ions in dilute equilibrium solutions have been calculated

by using Davies equation in the form

$$- \log f = \frac{Az^2 \sqrt{I}}{1 + a^0 B \sqrt{I}} - 0.2 Az^2 I$$

Activity ratios in soil solutions depend on the proportion of different exchangeable cations, but changes in the proportions alter the activity ratios differently in different soils. The difference may reflect different cation-exchange capacities of soils, or possibly, different strengths with which certain cations are adsorbed. Several workers have shown that the ratios of activities of ions in dilute equilibrium solutions may be useful chemical properties of the soil system (Schofield and Taylor, 1955a; 1955b; Schuffelen and Bolt, 1958; Taylor, 1958; 1960; Webster and Harward, 1959; Moss, 1963a; 1963b; Salmon, 1964a; 1964b; Beckett, 1964a; Tinker and Bolton, 1966). It appears that the use and measurements of ion ratios are, therefore, advantageous and less ambiguous than other approaches. Various methods for obtaining equilibrium soil solutions are described in the literature (Taylor, 1958; Webster and Harward, 1959; Matthews and Beckett, 1962; Dutt, 1962; Moss, 1963a; Salmon, 1964a; Beckett, 1964a). Moss (1963a) found that the values of $pK - \frac{1}{2}p(Ca + Mg)$ were constant for one soil over the entire moisture range studied whilst they were only constant over the field range of moisture for another two soils. The constancy of the value $pK - \frac{1}{2}p(Ca + Mg)$ indicates an undisturbed equilibrium (Taylor, 1958; Moss, 1963a; 1964a; Beckett, 1964a). Activity ratios like $\frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}}$ in dilute solutions at equilibrium with soil are independent over a specified range of total electrolyte concentrations (Schofield and Taylor, 1955; Taylor, 1958;

Matthews and Beckett, 1962; Moss, 1963b; Salmon, 1965) and both release and adsorption of potassium were shown to be functions of the potassium concentration of the equilibrium soil solution (Moss, 1963b). Schofield and Taylor (1955) have utilized the activity ratio concept to develop an expression known as the "lime potential". Woodruff (1955a; 1955b) has shown that the value of $pK - \frac{1}{2} pCa$ is a function related to the partial molar free energy of exchange of these ions, i.e. $\Delta F = 1364 (\frac{1}{2} pCa - pK)$. The importance of this value with respect to plant nutrition has been discussed (Woodruff, 1955c). The term $pK - \frac{1}{2} p(Ca + Mg)$ has been suggested as an intensity factor in measuring the potassium status of soils (Beckett, 1964a; 1964b; Tinker, 1964a; 1964b; Acquaye et al, 1967; Moss, 1964b; Salmon, 1963; 1965).

Recently the concept of ion ratios has been used on the assumption that these ratios measure the nutrient availability to plants. Heimann (1959) has emphasized the importance of sodium-potassium ratio in solution and concluded that under saline conditions antagonism is predominant. According to Zhukov (1963) if the soil is adequately supplied with nutrients, the best conditions for most crops will prevail when univalent (K and Na) and bivalent (Ca and Mg) cations are present in the soil solution in equal or nearly equal equivalent quantities. Wiklander (1966) studied nutrient uptake by growing plants in nutrient solutions of decreasing concentrations keeping the ion ratios constant. He concluded that dilution favours the adsorption of divalent as compared to that of monovalent cations. He also found that a very low Ca level in the solution exerts a depressive influence on Ca uptake and plant growth. Moss (1964b) investigated the effect of various fertilizer

treatments on soil solution composition and found a significant correlation of $\log K - \frac{1}{2} \log (Ca + Mg)$ in the plant and values of $pK - \frac{1}{2} p (Ca + Mg)$ in the soil solution. Salmon (1964b) reported a linear relationship between the concentration of Mg in grass and $\sqrt{\frac{a_{Mg}}{a_{Ca} + Mg}}$

in the equilibrium soil solution. Tinker (1964b) reported a relationship between yield response and $\frac{a_K}{\sqrt{a_{Ca} + Mg}}$ of the soils determined in the

presence of sufficient lime water to remove soluble aluminum. He obtained a better relationship between yield response and a unified activity ratio

$$\frac{(K^+)}{\sqrt{\{(Ca^{++}) + (Mg^{++})\} + P \sqrt[3]{(Al^{+++})}}}$$

called ARu, the activities being those found in the true equilibrium solutions.

It is well established that high concentrations of certain soluble salts may restrict germination and plant growth because of high osmotic pressure and reduction in water uptake. Attempts have been made to study the effect of cations either in solution or in the adsorbed phase on growth and chemical composition of plants. Elgabaly (1955) concluded that sodium, up to a given saturation percentage, may not itself have a depressing effect on the growth of barley. His results suggest the upper limit of adsorbed sodium in alkali soils at 15 per cent may not be justified from the nutritional point of view, as sodium stimulated barley growth at this percentage. The nature of the complementary ions and type of plants must also be considered when setting this limit. A high sodium saturation percentage, however,

depressed barley growth due to the unbalance among nutrients caused by differential uptake and depletion in nutrients (Elgabaly, 1955).

Berstein and Pearson (1956) found a decreasing yield of legumes with increasing exchangeable sodium percentage. They concluded that excessive sodium accumulation by roots may affect root function, particularly water adsorption and thus depresses yield. Elgabaly and Ghani (1958) observed a detrimental effect of increasing sodium saturation on the growth of peas and explained this effect on the basis of unbalance between nutrients caused by depletion of calcium and excessive adsorption of sodium. Toxic effect on barley plants caused by excessive concentration of sodium in salt affected soils has also been demonstrated by Elgabaly and Madkour (1965). Soils high in exchangeable sodium tend to be dispersed and may limit plant growth by reason of impaired water penetration, poor aeration or physical resistance to root growth (U.S. Salinity Laboratory Staff, 1954). Pálfi (1965) observed that high sodium content exerted a differential effect on uptake of nitrogen and phosphorus and depressed the plant yield. He also found that the presence of high concentration of sodium ions in nutrient medium impaired the uptake of ammonium ions by the rice plants. High sulfate ion concentrations will limit the uptake of calcium by plants and consequently the adsorption of sodium and potassium will be increased (U.S. Salinity Laboratory Staff, 1954). Thus the harmful effects of high sulfate concentrations may be related to a disturbance of optimum cation balance within the plant. There is evidence in the literature that high concentrations of sulfate may also antagonize phosphate uptake by plants (Pálfi, 1965). The data

presented by Ogata and Bower (1965) conclusively prove that sulfate reducing microorganisms are generally present in arid zone soils. Furthermore, their findings also revealed that when organic matter content is high in these soils (>5 per cent) sulfate reduction results in the formation of equivalent amounts of carbonates which upon reaction with soluble or exchangeable calcium and precipitation as CaCO_3 causes an increase in the exchangeable sodium percentage. This may evidently affect plant growth.

From the foregoing it would appear that an excessive concentration of sodium sulfate, a dominant soluble salt in the solonetzic soil under study, will depress plant growth. In contrast, Cairns (1962a) obtained results which suggest that sodium sulfate added to surface samples of Thin Duagh loam soil had a beneficial effect on the growth of crops in pots. The quantity of sodium added at the high level exceeded that found at any depth of the soil sampled. Plants grown on soil to which no sodium sulfate was added turned yellow while those grown on the treated soil were dark green in colour. It has also been postulated that the effect was not a direct crop response to sulfur (Cairns, 1962a). In the greenhouse when the crop was grown on the solonetzic soil under study, a nutritional disorder was developed which was diagnosed as a nitrogen deficiency (Cairns et al, 1962). The application of nitrate nitrogen to the soil allowed the production of repeated crops at a level comparable with that of the geographically associated chernozemic soil. Other studies on these soils suggest that deep ploughing method of amelioration holds more promise than methods based on the application of commonly

suggested amendments, e.g. gypsum, sulfur, (Cairns, 1961; 1962b).

In view of the literature cited in this section, it appears that a nutritional aspect may have a significant bearing on the low productivity of the solonetzic soil. It is, therefore, hypothesized that in spite of the high levels of salinity and other factors, certain undesirable cation ratios in soil solution might also be a contributory factor affecting the productivity of the solonetzic soil under study. However, the ratios appear favourable for plant growth in the geographically associated chernozemic soils. Therefore, a study of various cation ratios and other related properties as affected by change in moisture content in the foregoing two soils was felt warranted. It was considered that this would be the most logical approach in order to gain a better understanding of the nutritional status of soil solutions based on physical-chemical considerations. The investigation described in this chapter deals with this aspect of the problem. The four sub-topics which constitute this chapter are arranged in a logical sequence for the convenience of presenting data. The first two deal largely with the characterization of soils and preliminary greenhouse experiment and the last two are concerned with various aspects of cation ratios and related properties.

Characterization of Soils

Soils Used in Study:

Two profiles, a Black Solonetz (Duagh silt loam) and an Eluviated Black Chernozem (Malmo silt loam), both located at Vegreville

Experimental Sub-station, were selected for this study. These soils occur on the same parent material which consists largely of saline lacustrine silty clay loam and clay (Bowser et al, 1962). The soil profiles were exposed and samples were collected on a horizon basis. The designations of soil horizons are in accordance with the nomenclature recommended by the National Soil Survey Committee of Canada (1963). The location of the sampled profiles, horizons and their thickness are shown in Fig. 5.

Throughout this chapter the soils hereafter will be referred to by their type names. Following sampling, the soils were brought into the laboratory, air dried at room temperature and ground to pass through a 2 millimeter sieve. The prepared samples were stored in glass containers until needed for analysis.

Experimental Methods:

(1) Chemical analysis: The pH of saturated pastes was measured with a Beckman Expanded Scale pH meter, equipped with a glass and a calomel electrode. For electrical conductivity determinations, saturated pastes were prepared (U.S. Salinity Laboratory Staff, 1954) and saturation extracts were obtained using pressure filtration funnels fitted with Metrical filters. The electrical conductivity of the extracts was measured with a direct reading Solu-bridge Model RD-26. The soluble cations Na, K, Ca and Mg in these saturation extracts were determined with a Perkin-Elmer Atomic Adsorption Spectrophotometer Model 303 connected to a Sargent recorder Model SR. The experimental conditions were those specified in the analytical methods manual (1966). The CO_3 and HCO_3 in the saturation extracts were determined with a radiometer

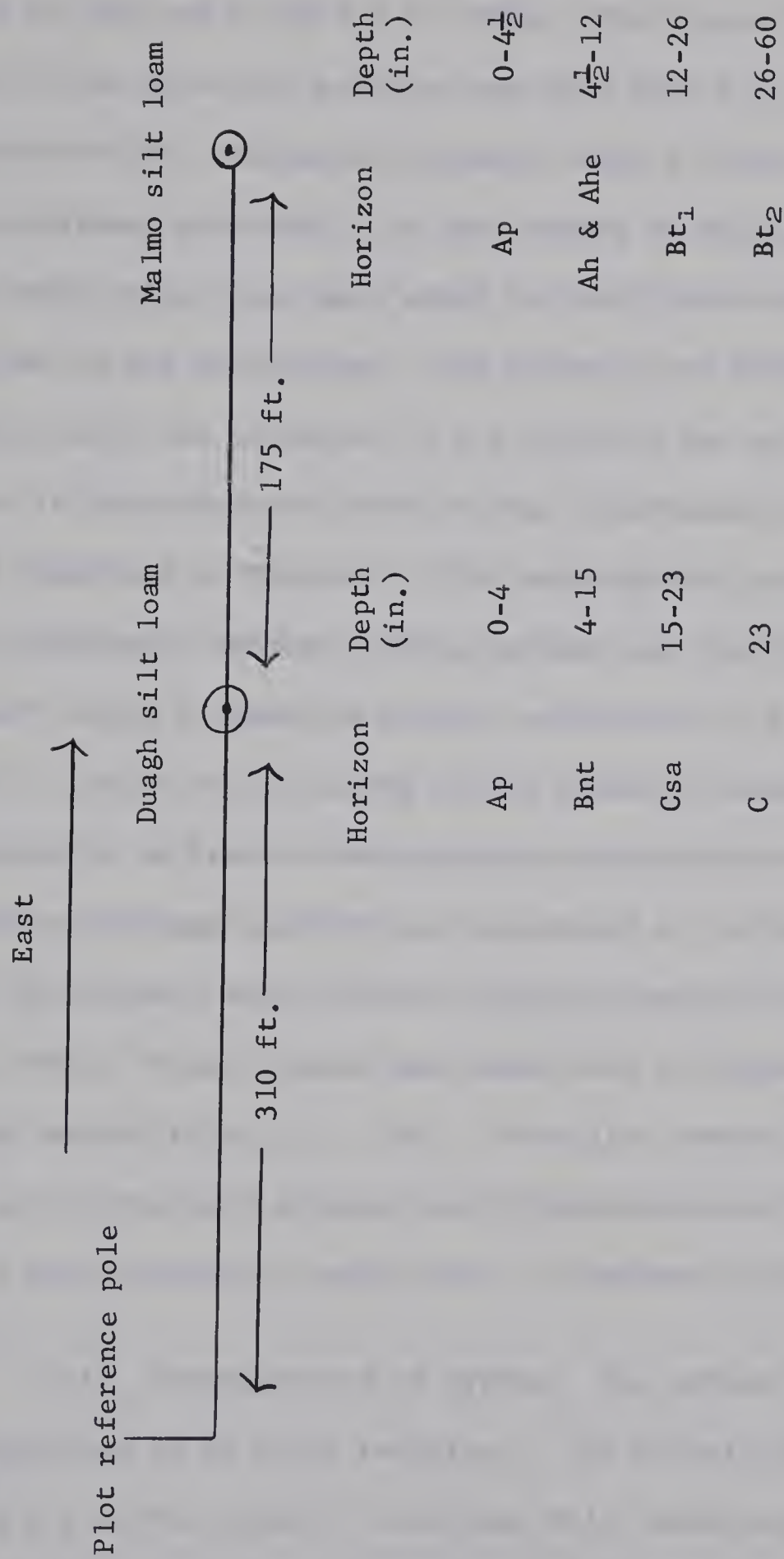


Fig. 5 Soil Profiles under study and their location at Vegreville

titrator type TTT1b No. 37131 (Copenhagen) equipped with a glass electrode and a calomel half cell. The solution was titrated with 0.01 M HCl to pH 8.0 for CO_3 and to pH 4.4 for HCO_3 . The CO_3 was considered to be absent if the pH of the solution was less than 8.0. The Cl was also measured with the radiometer titrator using a silver and a mercuric sulfate-calomel electrode. To each sample of solution, 25 ml. of 50 per cent acetic acid were added to facilitate coagulation of fine particles in the precipitate. The solution was titrated with 0.001 M AgNO_3 solution until the potential of the solution was equal to a blank. Sulfate in the saturation extracts was determined by the electro-metric method described in Chapter 2. The exchangeable cations were calculated as the difference between soluble cations and "soluble plus extractable cations", using 1M ammonium acetate solution as the extractant adjusted to pH 7. The Na, K, Ca and Mg in the ammonium acetate extracts were determined by an Atomic Adsorption Spectrophotometer as described before. The cation exchange capacity was determined as outlined by the A.O.A.C. (1955) and organic matter by wet-oxidation method (U.S. Salinity Laboratory Staff, 1954). Total organic and ammoniacal nitrogen was determined by Kjeldahl method (A.O.A.C., 1955). Distilled ammonia was collected in 4 per cent boric acid solution and titrated against standard H_2SO_4 using a mixed indicator (methyl red - bromcresol green).

(ii) Determination of gypsum: The gypsum content of the soils was determined by an X-ray technique. The principle of this method is not new but to the author's knowledge this technique has not been widely used by soil scientists. Therefore, a detailed description of the method

is warranted.

The precise determination of gypsum in soils is difficult because of the inherent errors involved in the extraction of this mineral by water (U.S. Salinity Laboratory Staff, 1954). Several methods suggested in the literature (Bower and Huss, 1948; U.S. Salinity Laboratory Staff, 1954; Lagerwerff et al, 1965) appear unsatisfactory for solonchic soils containing large amounts of sodium sulfate. Thus there is a reason for developing a satisfactory method for a quantitative determination of gypsum.

The technique described here utilizes the principle that each salt in soils should produce its own characteristic diffraction pattern independently of others and that the relative intensities of the patterns are related to the proportion of the salt present. In practice, the average recorded height of one prominent reflection from each salt is usually sufficient for model estimates, provided (i) the instrument has been calibrated with standard samples to agree with established intensity-concentration curves, (ii) no significant superposition by peaks of other constituents is encountered, and (iii) correction is made for background intensity.

All work was done with a Norelco Geiger Counter, X-ray Diffraction Spectrometer using copper radiation, nickel filter and a scanning speed of $1^{\circ} 20$ per 2 minutes. The tube was set at 35 kv and 15 ma. A scale factor of 8 and time constant of 4 were selected on the recorder.

The procedure for preparing powder samples (300 mesh) was essentially the same as outlined by Tatlock (1966). Samples were mounted

in rectangular aluminum holders. In preliminary experiments powdered samples of the following were scanned from 2° to $52^{\circ} 2\theta$: (i) soil under study, (ii) soils + gypsum, (iii) soils + gypsum + sodium sulfate + magnesium sulfate, and (iv) gypsum + sodium sulfate + magnesium sulfate.

Potassium chloride was added to each sample as an internal standard. It was found that the X-ray diffraction peaks of gypsum and potassium chloride were not significantly superimposed upon those of other salts or clay minerals present in the soils. The most intense diffraction peaks of gypsum and potassium chloride appeared at about 11.71° and $28.41^{\circ} 2\theta$ respectively (Fig. 6). These peaks were considered best for quantitative estimation of gypsum in subsequent studies. Results of the preliminary experiments also suggested that no gypsum was present in any horizon of the Malmo silt loam soil. Consequently, Bt_1 horizon of this soil was used as matrix material in preparing standard samples. Each standard sample contained 2 per cent potassium chloride and varying proportions (0 - 4.0 per cent) of gypsum to cover the expected range in the soil. The selected diffraction peaks for gypsum and potassium chloride were scanned (Fig. 6) and the instrument was set on the peak of maximum intensity and the time required to register a certain fixed number of counts was recorded. The background intensity for each peak was taken as the average of four measurements, two on each side of the peaks (Fig. 6). The ratios of counts per minute for gypsum and potassium chloride, after being corrected for background, were plotted against gypsum concentration (Fig. 7). For determination of gypsum in the soils under study a similar procedure was adopted and concentration was read from the calibration

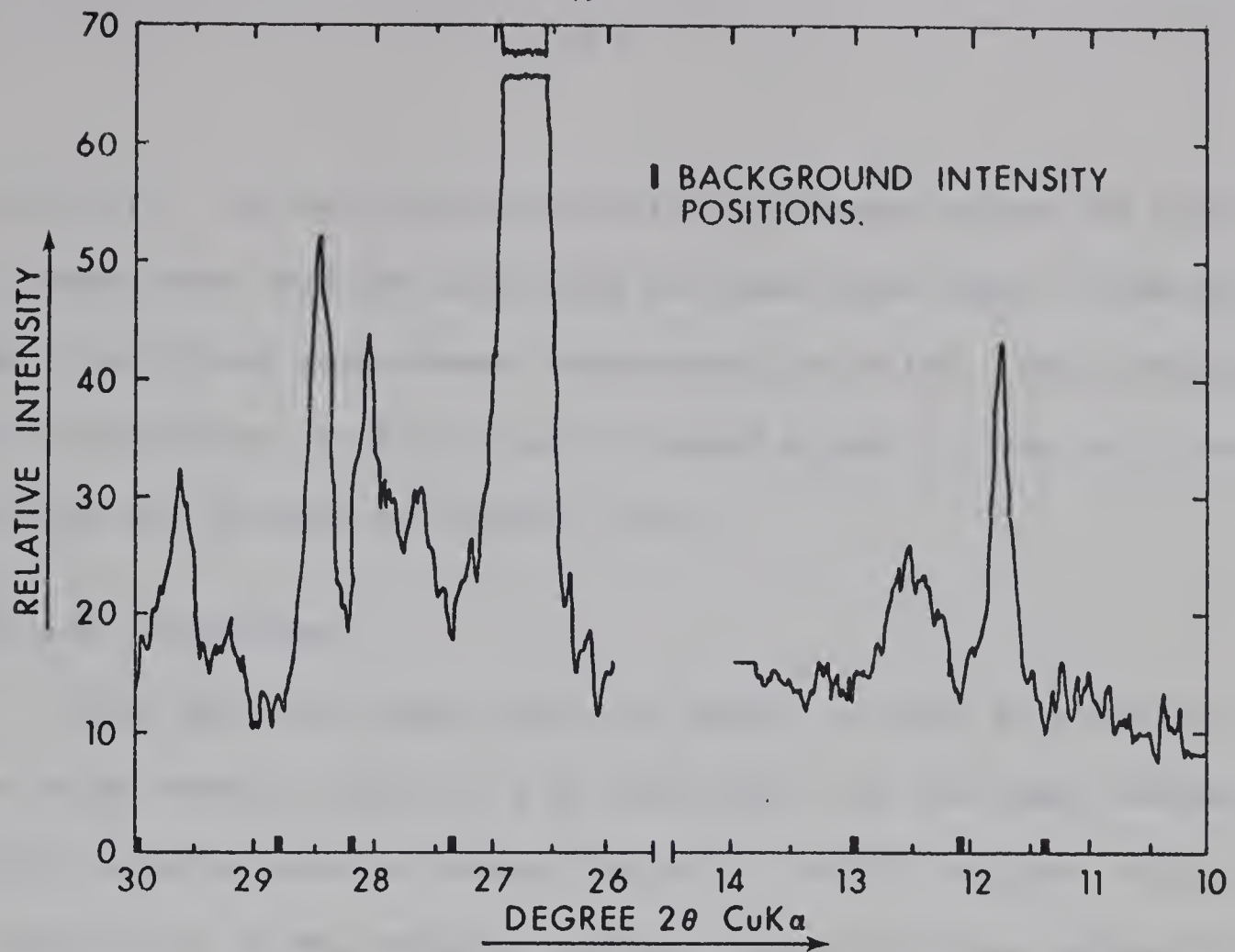


Fig. 6. Diffraction pattern of the Malmo silt loam Bt₁ horizon containing gypsum and potassium chloride

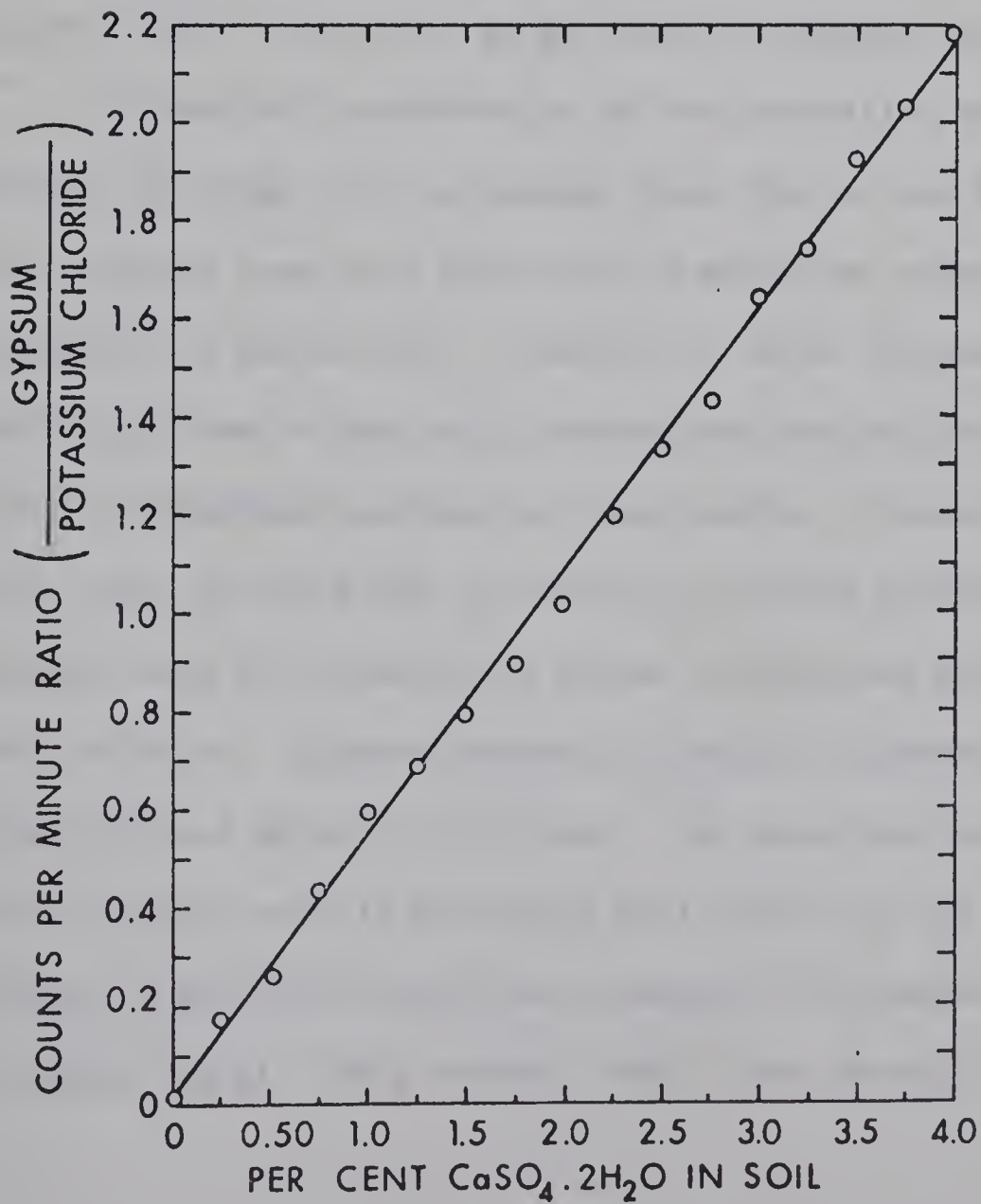


Fig. 7. Calibration curve for gypsum determination in soil

curve (Fig. 7). In all determinations four different mounts for each powder sample were used and each mount was read three times. Thus the average of all these measurements represented one value. The technique appears satisfactory, as 91 per cent of added gypsum in Duagh silt loam Csa horizon was obtained in recovery tests.

Results and Discussion:

Both Malmo and Duagh soils are acidic in their Ap horizons, and the Malmo remains acidic to a 26 inch depth, but the Duagh becomes moderately alkaline below 4 inches (Table 7). Acidic horizons reflect base unsaturation of the exchange complex, higher pH values reflect higher sodium and/or calcium contents. The results are in agreement with those of Cairns (1961) and Bowser et al (1962), reported for similar soils.

Electrical conductivity of the saturation extract of surface Ap horizon of Duagh soil is greater than that of any horizon of Malmo, but is slightly less than the value (4 mmhos/cm) established as the criterion for a saline soil. There is a rapid increase of electrical conductivity from surface Ap to subsurface Bnt horizon of Duagh soil, and then it remained constant at lower depths. There is an abundance of soluble salts in the Duagh as compared to Malmo profile. Soluble carbonates were not detected in either profile and both had very little soluble chloride. Highest amounts of soluble bicarbonate were detected in Duagh Bnt and Malmo Bt₁ horizons. The data show sodium sulfate is the dominant soluble salt in the Duagh soil (Table 7) and this is in accordance with results reported elsewhere for similar soils (Cairns, 1961; Bowser et al, 1962; Arshad, 1964). The amounts of soluble calcium

TABLE 7

Some Chemical Characteristics of the Soil under Study

Soil type	Horizon	Depth (in.)	pH (Sat. paste)	EC mmhos/cm (Sat. extract)	Saturation %	Exchangeable cations *			
						Na ⁺	me./100 gm soil K ⁺	Ca ⁺⁺	Mg ⁺⁺
Duagh silt loam	Ap	0-4	5.8	3.30	56.6	5.06	1.40	5.6	7.1
	Bnt	4-15	7.3	11.3	66.2	8.31	0.99	16.0	12.5
	Csa	15-23	8.2	12.5	70.8	6.55	0.36	53.9	11.5
	C	23-	8.2	12.5	74.6	6.67	0.35	60.5	11.7
Malmo silt loam	Ap	0-4 $\frac{1}{2}$	5.9	0.66	79.1	0.32	3.73	19.7	11.5
	Ah & Ahe	4 $\frac{1}{2}$ -12	5.9	0.68	47.3	0.46	4.44	12.2	10.2
	Bt ₁	12-26	6.9	1.50	56.7	0.81	3.58	21.1	7.9
	Bt ₂	26-60	7.6	2.95	40.1	0.85	0.37	29.1	6.1

* Ammonium acetate extractable-soluble

** Summation of exchangeable cations

*** Exchangeable sodium percentage = $\frac{\text{Exchangeable Na}^+}{\text{Detd. C.E.C.}} \times 100$

TABLE 7 (Continued)

Exch. Ca ⁺⁺ /Mg ⁺⁺	C.E.C.		Soluble cations and anions							ESP***	Organic matter %	Nitrogen %	Gypsum %
	Calcd.** me./100 gm soil	Detd. me./100 gm soil	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	SO ₄ ⁻⁻	HCO ₃ ⁻	Cl ⁻				
0.08	19.2	51.1	2.08	0.04	0.11	0.20	2.28	0.17	0.03	9.9	9.56	0.45	-
1.3	37.8	36.4	8.70	0.05	1.14	2.00	11.40	0.64	0.02	22.8	3.28	0.19	0.22
4.7	72.2	36.6	10.13	0.05	1.44	1.92	14.23	0.17	0.03	17.9	0.88	0.07	2.79
5.2	79.2	38.2	11.34	0.05	1.48	1.90	15.38	0.13	0.04	17.5	0.87	0.07	3.42
1.7	35.3	61.6	0.14	0.14	0.13	0.13	0.24	0.26	0.05	0.52	14.98	0.77	-
1.2	27.2	44.5	0.11	0.09	0.05	0.05	0.12	0.14	0.03	1.03	6.64	0.35	-
2.7	33.4	34.8	0.45	0.11	0.23	0.13	0.42	0.47	0.03	2.33	1.69	0.10	-
4.8	36.3	30.0	0.61	0.10	0.32	0.29	1.06	0.12	0.01	2.83	0.61	0.06	-

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Date		Time		Location		Remarks	
Day	Month	Hour	Min	Place	Altitude	Notes	Remarks
1	Jan	10	00	1000	1000	1000	1000
2	Jan	11	00	1000	1000	1000	1000
3	Jan	12	00	1000	1000	1000	1000
4	Jan	13	00	1000	1000	1000	1000
5	Jan	14	00	1000	1000	1000	1000
6	Jan	15	00	1000	1000	1000	1000
7	Jan	16	00	1000	1000	1000	1000
8	Jan	17	00	1000	1000	1000	1000
9	Jan	18	00	1000	1000	1000	1000
10	Jan	19	00	1000	1000	1000	1000
11	Jan	20	00	1000	1000	1000	1000
12	Jan	21	00	1000	1000	1000	1000
13	Jan	22	00	1000	1000	1000	1000
14	Jan	23	00	1000	1000	1000	1000
15	Jan	24	00	1000	1000	1000	1000
16	Jan	25	00	1000	1000	1000	1000
17	Jan	26	00	1000	1000	1000	1000
18	Jan	27	00	1000	1000	1000	1000
19	Jan	28	00	1000	1000	1000	1000
20	Jan	29	00	1000	1000	1000	1000
21	Jan	30	00	1000	1000	1000	1000
22	Jan	31	00	1000	1000	1000	1000

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* Ar

** Si

** E:

and magnesium are generally small relative to sodium in both soils, but not insignificant in determining the chemical character of these soils. Soluble potassium in Duagh soil is low and in Malmo is like-wise especially in the Bt₂ horizon. The saturation percentage of soils may vary due to differences in the amount and kind of clay minerals, organic matter, soil texture, and salts present in the soil (U.S. Salinity Laboratory Staff, 1954). For Duagh soil the saturation percentage ranges from 56.6 to 74.6 and for Malmo from 40.1 to 79.1 per cent. The saturation percentages reported in Table 7 were used to convert the concentration of soluble salts (me./l) to that in terms of soil weight (me./100 gm.).

In saline and alkali soils, determination of exchangeable calcium and magnesium are confounded by solution of solid phase gypsum and carbonates in the extracting solution. Bower et al, (1952) found about 17 me./l of calcite, 9 me./l dolomite and 1 me./l of magnesite soluble in the neutral 1M ammonium acetate extracting solution used. The amounts and proportions of solid salts dissolved may be expected to vary depending on the crystal phase present and the experimental conditions. In Table 7 exchangeable calcium and magnesium are reported for Duagh soil even though it is realised that a part of these cations is due to the solution of solid phase salts in the extracting solution. The cation exchange capacity of Csa and C horizons of Duagh soil determined by summation differs from that found by direct determination (Table 7). Obviously this can be attributed to the solution of solid phase salts in the ammonium acetate extract and are added to the exchangeable cations. Similar observations have also been described elsewhere (Kelley, 1948;

Bowser et al, 1962, Arshad, 1964). The high cation exchange capacity of surface Ap horizons of both soils can be attributed to the presence of high organic matter content (Table 7). Exchangeable potassium is greater in the surface horizons of both soils than at lower depths. In general there are much higher levels of exchangeable potassium in Malmo than in Duagh soil whereas the reverse is true for exchangeable sodium. The relatively high exchangeable sodium content in the B as compared to the A or C horizons of the Duagh is in accordance with other workers' findings on similar soils (Bowser, et al, 1962; Arshad, 1964). Exchangeable magnesium in the Duagh profile follows a trend very similar to exchangeable sodium. Exchangeable calcium tends to be highest in the lower horizon of both profiles. The exchangeable calcium-magnesium ratios are relatively wide in lower and narrower in the upper horizons of both profiles. This is, however, more marked in the Duagh soil. The narrower ratios may result in magnesium toxicity (Kelley, 1951); however, Halstead et al (1958) found no effect of calcium-magnesium ratios on plant growth. The Malmo soil contains high organic matter and nitrogen relative to the Duagh, although, the pattern of distribution in the profiles is similar. There is a marked decrease of organic matter and nitrogen contents immediately below the surface Ap horizons of both soils. The Malmo soil is essentially free of gypsum throughout its solum. There is no gypsum in Ap, a small amount in Bnt and considerable amounts in the C horizons of the Duagh profile (Table 7).

Greenhouse Experiment

Materials and Methods:

Air dried (≤ 2 mm) surface soil of the Duagh series was used in this study. To exclude any possible microbiological effect on plant growth for certain treatments, soil was sterilized by Gamma radiation. Samples were placed in double polyethylene bags which were then closed tightly against the soil with strings. They were subjected to Gamma rays derived from a CO^{60} source in a Gamma cell 220. Each sample received a total exposure of approximately 2.25 mega rads in three hours. Samples were returned to the laboratory and used in the greenhouse experiment. Five hundred gram lots of air dry soil were placed in undrained plastic cartons. For sterilized soils, cartons were washed with mercuric chloride and then repeatedly washed with sterilized distilled water. The soil was wetted by adding distilled water (sterilized distilled water for irradiated soils) to bring it to 40 per cent moisture level at the start; thereafter moisture was allowed to fluctuate between 25 and 35 per cent during the experiment. Gateway barley was seeded, 30 kernels in each pot and the soil was covered with 5.0 gm of perlite to prevent crusting. After emergence, the crop was thinned to 12 plants per pot. Sodium sulfate was added to give salt contents of 5 (untreated), 12, 16 and 20 me. of soluble sodium per 100 gm of soil. Nitrogen was added in the form of sodium nitrate (treatment E) and ammonium sulfate (treatment F), half (350 ppm) to the first crop and half to the second. All treatments were supplied in solution, as a substitute for a portion of the water, in three equal instalments on the first day and at three day intervals. Artificial light

was provided from 6 a.m. to 9 p.m. every day. A randomized block design with four replications was used for this study. After 32 days the plants were harvested, dried at 70°C overnight and the dry weight was recorded. A second crop was grown in the same pots following the procedure outlined above, except no further sodium sulfate was added. The crop was harvested after 29 days and dry weight determined.

Results and Discussion:

The effects of added sodium sulfate and nitrogen on the yield of barley are reported in Table 8 and the appearance of plants prior to harvesting of the first crop is shown in Fig. 8. The yields of both crops decreased significantly with increasing rates of sodium (treatment A vs. B, C, D and treatment G vs. H, I). Cairns (1962a) found that the yield of the first barley crop decreased with increasing levels of sodium, but not significantly. However, the yield of the second crop was significantly higher where sodium sulfate had been added than where none was added (Cairns, 1962a). It is obvious that the data reported in Table 8 do not bear out this effect, but rather the results demonstrate the detrimental effects of increasing sodium levels in the soil in accordance with findings reported elsewhere (Elgabaly, 1955; Bernstein and Pearson, 1956; Elgabaly and Ghani, 1958; Elgabaly and Madkour, 1965; Pálfi, 1965). Irradiation significantly increased the yield of barley on non-treated soil. Gamma radiation of soils increases the availability of nitrogen and phosphorus in many soils (Stanovick, et al, 1961; Eno and Popenoe, 1963; Cummins and McCreery, 1964). This will be a significant nutritional factor when plants are grown on irradiated soils and possibly explains the higher

TABLE 8

The Effect of Various Treatments on the Dry Matter Yield
of Barley Grown on Duagh Silt Loam Surface Soil in the
Greenhouse

Treatment	Barley yield (gm/pot)				
	First crop	Stat. sig.*	Second crop	Stat. sig.*	
A	5 me. Na/100 gm soil	1.15	0.81	d	c
B	12 " " "	0.73	0.19	e	d
C	16 " " "	0.61	0.12	e	de
D	20 " " "	0.53	0.06	ef	e
E	700 ppm NO ₃ -N	1.93	1.24	b	b
F	700 ppm NH ₄ -N	2.14	1.46	a	a
G**	5 me. Na/100 gm soil	1.46	1.20	c	b
H**	12 " " "	0.70	0.13	e	de
I**	20 " " "	0.37	0.04	f	e

* Stat. sig. means "statistical significance at the 0.05 level" as determined by Duncan's Multiple Range test. Mean followed by letter "a" is significantly different from those not having "a", those followed by "b" are significantly different from those not having "b", etc.

** Gamma radiated soils



Fig. 8 Influence of sodium sulfate and nitrogen on growth of first crop of barley on Duagh silt loam surface soil (for treatments see Table 8)

yield of barley from this treatment (treatment A vs. G). The data also show that nitrogen applied in the form of ammonium sulfate was significantly more effective than that applied in the sodium nitrate form. This difference can probably be attributed to the 5 me. of sodium/100 gm soil contained in sodium nitrate.

In summary the foregoing results do not support the earlier findings by Cairns (1962a). However, Cairns (1962a) used a Thin Duagh loam soil rather than the Duagh silt loam that was used in the present study and this may be the reason for the different results. Kelley (1951) however, states "the alteration in ratios of the various ions present when a sodium salt is added may also have something to do with the effect of growth." It appears that possibly for this reason and others the

addition of sodium sulfate resulted in a significant decline of crop growth on the soil under study.

Equilibrium Cation Ratios and Related Properties

Materials and Methods:

Air dried samples (≤ 2 mm) of the Duagh and Malmo soils were used in this study. A number of their chemical characteristics have been described previously in this chapter. Moisture determinations were made at the air dry, 15 atm, 1/3 atm and saturation percentage (U.S. Salinity Laboratory Staff, 1954). In addition a moisture level at 100 per cent and the average of moisture contents at 1/3 and 15 atm were also included in this study. The latter for convenience is referred to as $\frac{1/3 + 15}{2}$ atm percentage. The moisture percentages are shown in Table 9.

Equilibration and Extraction of Soil Solutions: The experiments were designed to determine the ion concentrations and ion ratios of solutions which, on being shaken with the soil adjusted to different moisture levels, suffered no change and could therefore be assumed to be in equilibrium with the soil. Fifty gm samples, in duplicate, of uniformly mixed soil, were placed in 300 ml Erlenmeyer flasks to which were added different amounts of distilled water to bring them to various moisture contents on an oven-dry weight basis (Table 9). These samples were thoroughly mixed and the flasks were covered with parafilm paper to avoid moisture loss and allowed to stand, or, if in suspension shaken for a 24 hour period at room temperature ($\sim 22^{\circ}\text{C}$). Each was then shaken with a series

TABLE 9

Moisture Characteristics of the Two Soil Profiles under Study (oven dry basis)

Soil type	Horizon	Depth in.	Per cent moisture			
			Saturation	1/3 atm	$\frac{1/3 + 15 \text{ atm}}{2}$	15 atm Air dry
Duagh silt loam	Ap	0-4	56.6	42.4	35.1	27.8 6.98
	Bnt	4-15	66.2	38.1	31.0	24.0 5.15
	Csa	15-23	70.8	32.5	25.4	18.4 4.36
	C	23-	74.6	35.1	27.9	20.6 4.21
Malmo silt loam	Ap	0-4 $\frac{1}{2}$	79.1	42.3	34.5	26.6 14.6
	Ah & Ahe	4 $\frac{1}{2}$ -12	47.3	31.2	26.6	22.0 6.43
	Bt ₁	12-26	56.7	32.1	27.1	22.2 4.50
	Bt ₂	26-60	40.1	23.7	17.6	11.6 2.38

of solutions of different ion concentration and ratios. The concentrations of ions in these solutions covered a wide range bracketting the concentration in the saturation extracts (Table 7), so that values in true equilibrium solution would be located in this range. In order to get sufficient extract for analysis, the total moisture volume in each flask (including the water added to produce the various moisture contents) was brought up to 85 ml by adding calculated amounts of solutions. The samples were shaken for one hour as it was established in subsidiary experiments described later, that acceptable equilibrium conditions were attained in this period. The suspensions were then centrifuged for one hour in a RC-2 Sorvall Superspeed Automatic Refrigerated centrifuge at 17,000 rpm. During centrifugation the temperature was maintained at $\approx 22^{\circ}\text{C}$. The solutions were filtered through Whatman No. 42 paper and the clear solutions were analysed for cations and anions.

Of the foregoing solutions, that which changed the least in concentration on shaking with a soil at a given moisture content was selected. This solution was used to help determine the composition of six or eight other solutions, each containing a slightly different proportion of the various cations and anions found in the extracts at each moisture content so that the ion concentration included the value expected in the true equilibrium solution. The experiments were performed as described and the clear solutions were analysed.

The true equilibrium ion-concentration is that concentration which does not change when the solution is equilibrated with the soil. This was estimated by plotting the ion concentrations for the solutions

against the concentrations for the corresponding filtrates after equilibration. The intersection of the line of best fit for these points with a line of slope 1.0 drawn through the origin was taken as the true equilibrium ion concentration. From these concentrations, equilibrium cation ratios and equilibrium ionic strengths were calculated. Solutions of the same composition as determined in true equilibrium solutions were made and equilibrated with soils at corresponding moisture contents (100 per cent, 1/3 atm, $\frac{1/3 + 15}{2}$ atm, 15 atm and air dry) following the procedure described before. The pH values of the suspensions were determined. The suspensions were then centrifuged, filtered and the pH and electrical conductivity of the clear solutions were determined.

The method for determining cations, anions, pH and electrical conductivity were essentially the same as described previously in this chapter.

Results and Discussion:

Equilibration Time and Reliability of Technique: The ionic strength of each equilibrium solution was calculated using equation $I = \frac{1}{2} \sum CZ^2$ where C denotes concentration in moles per litre and Z the valence. The ions in these solutions included Ca^{++} , Mg^{++} , Na^+ , K^+ , SO_4^{--} , HCO_3^- and Cl^- . For Duagh soil, the ionic strength of the various equilibrium solutions is regarded as being too high for the calculation of activity coefficients. Consequently, concentration ratios are used throughout (Table 12). However, for the Malmo soil these are expressed as activity ratios (Table 13), the activities being determined from the measured concentrations and

calculated activity coefficients. The activity coefficients (f) were calculated using the equation described previously in this chapter. For convenience the ratios are expressed in negative logarithmic form. Thus the letters 'P' and 'p' refer to negative logarithm of concentrations and activities respectively.

To ensure that the solid and solution phases are in equilibrium state it is of paramount importance that soil samples be equilibrated long enough to allow complete reaction. Under equilibrium conditions the cation ratios would be expected to remain constant with time. A series of experiments were carried out to determine the true equilibrium cation ratios for various periods of shaking ranging from 15 minutes to 4 hours. Samples from one horizon of the Duagh and Malmo soils were adjusted to two moisture contents for this purpose and the results are reported in Tables 10 and 11. It would appear that the ratios were virtually constant with time particularly after a one hour shaking period for both soils at the two moisture contents studied. This provides evidence that the equilibrium between solid and solution phases was attained. Consequently, a one hour equilibration period was used throughout the remainder of this study.

It is obvious that the technique described is satisfactory for determining the ion ratios in true equilibrium solutions for saline and/or alkaline as well as non-saline soils adjusted to various moisture contents. It also permits determinations of soil solution composition at a moisture content in the field moisture range without the use of any special extraction equipment. Because salts were present in the solid form in Duagh soil, it was reasoned that it would be meaningless to

TABLE 10
Effects of Shaking Time on Cation Concentration Ratios in Duagh Silt Loam Csa Horizon

Time in hours	PK- $\frac{1}{2}$ P (Ca + Mg)	PK-PNa	PCa-PMg	$\frac{1}{2}$ PCa-PNa	$\frac{1}{2}$ PMg-PNa	PNa- $\frac{1}{2}$ P (Ca + Mg)
			Moisture 70.8 per cent			
1/4	2.42	2.39	0.141	0.152	0.081	0.037
1/2	2.42	2.35	0.124	0.113	0.091	0.030
1	2.42	2.35	0.126	0.113	0.090	0.031
2	2.42	2.35	0.126	0.109	0.091	0.033
4	2.42	2.35	0.126	0.113	0.091	0.033
			Moisture 25.4 per cent			
1/4	2.38	2.59	0.290	0.448	0.302	-0.213
1/2	2.37	2.60	0.285	0.445	0.302	-0.211
1	2.37	2.60	0.287	0.443	0.299	-0.209
2	2.37	2.60	0.287	0.443	0.299	-0.209
4	2.37	2.60	0.277	0.443	0.300	-0.212

TABLE 11
Effects of Shaking Time on Cation Activity Ratios in Malmo Silt Loam Bt₁ Horizon

Time in hours	$\text{pK}-\frac{1}{2}\text{p}$ (Ca + Mg)	pK-pNa	pCa-pMg	$\frac{1}{2}\text{pCa-Na}$	$\frac{1}{2}\text{pMg-pNa}$	$\text{pNa}-\frac{1}{2}\text{p}$ (Ca + Mg)
				Moisture 56.7 per cent		
1/4	1.41	0.592	-0.231	-0.719	-0.604	0.821
1/2	1.42	0.616	-0.231	-0.702	-0.586	0.803
1	1.42	0.618	-0.240	-0.704	-0.584	0.804
2	1.43	0.622	-0.240	-0.709	-0.589	0.809
4	1.42	0.616	-0.231	-0.702	-0.586	0.803
				Moisture 27.1 per cent		
1/4	1.44	0.612	-0.161	-0.710	-0.603	0.825
1/2	1.45	0.623	-0.171	-0.710	-0.625	0.823
1	1.44	0.609	-0.165	-0.718	-0.636	0.833
2	1.47	0.635	-0.172	-0.718	-0.632	0.831
4	1.45	0.616	-0.165	-0.718	-0.636	0.833

determine equilibrium conditions in dilute equilibrium solutions as has been done for non-saline soils by various workers (Taylor, 1958; Webster and Harward, 1959; Matthews and Beckett, 1962; Moss, 1963a; 1963b; 1963c; Beckett, 1964a; 1964b; Tinker, 1964a; Salmon, 1964a; 1964b; 1965; Tinker and Bolton, 1966). Furthermore, the prediction of equilibrium concentrations on the basis of solubilities would be difficult because of the variety of salts present and the effect of other factors such as ionic strength on solubilities (Davies, 1962). Therefore, predicting equilibrium by computer methods, which also involves a series of approximations does not appear feasible (Dutt, 1962; Dutt and Doneen, 1963; Dutt, 1964; Paul et al, 1966). The technique described here has also been reported elsewhere for the Duagh soil sampled during the summer of 1963 (Khan and Webster, 1966).

Variation in Concentration of Ions with Change in Soil Moisture: Increase in soil moisture resulted in decreased concentrations of ions at equilibrium with the exception of calcium in the sub-surface horizons of the Duagh soil (Table 12 & 13). Results of Reitemeier (1946) and others (Kelley, 1951; U.S. Salinity Laboratory Staff, 1954; Moss, 1963a; 1963c; 1964a; Paul et al, 1966; Khasawneh and Adams, 1967) also suggest that the concentration of ions in soil extracts decrease with increased moisture content. However, the increase of moisture in the sub-surface horizons of the Duagh soil resulted in dissolution of solid gypsum thereby increasing the concentration of calcium in equilibrium solutions (Table 12). The amount of gypsum present in Bnt, Csa and C horizons of the Duagh soil is reported in Table 7. Based on these data it would appear that some gypsum

TABLE 12

Change of Ion Concentrations, Cation Concentration Ratios and Other Properties of Duagh Soil Equilibrium Solutions with Change in Moisture Content

Moisture (%)	pH (Suspension)	pH (filtrate)	Concentrations of ions mole/l x 10 ³						
			Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	SO ₄ ⁻⁻	HCO ₃ ⁻	Cl ⁻
Ap (0 - 4")									
7.0	5.9	6.7	78	1.07	1.45	2.88	43	4.07	0.94
27.8	6.0	6.6	50	0.94	1.13	2.44	28	3.68	0.86
35.1	5.9	6.5	47	0.90	1.13	2.28	26	3.59	0.79
42.4	5.9	6.4	43	0.85	1.12	2.12	24	3.42	0.72
56.6	5.9	6.3	37	0.74	1.01	1.78	20	3.07	0.60
100	6.1	6.3	18	0.44	0.32	0.76	9	2.00	0.24
Bnt (4 - 15")									
5.2	7.3	8.1	447	1.26	3.91	34.7	261	10.05	0.65
24.0	7.5	8.2	240	0.89	7.08	21.0	144	10.64	0.63
31.0	7.5	8.2	209	0.79	7.65	19.1	129	10.99	0.57
38.1	7.4	8.2	204	0.79	8.14	19.1	122	10.35	0.51
66.2	7.4	7.9	131	0.68	8.59	15.1	86	9.73	0.30
100	7.5	8.0	88	0.60	8.61	10.7	62	6.80	0.16
Csa (15 - 23")									
4.4	8.0	8.0	813	0.87	2.17	69.2	484	4.20	1.25
18.4	8.1	8.1	331	0.65	5.99	18.6	180	3.72	0.92
25.4	8.1	8.0	234	0.62	7.14	13.8	141	3.29	0.86
32.5	8.1	8.0	224	0.59	7.77	13.8	134	3.12	0.79
70.8	8.0	7.9	143	0.58	10.14	13.6	101	2.36	0.41
100	8.0	7.9	99	0.54	10.48	12.7	76	1.82	0.15
C (23" -)									
4.2	8.1	8.0	776	0.98	2.27	72.4	467	2.50	2.22
20.6	8.2	8.1	276	0.79	4.67	16.6	200	2.11	1.18
27.9	8.2	8.1	240	0.76	6.65	15.1	144	2.05	1.10
35.1	8.2	8.1	182	0.72	7.50	13.3	128	1.99	1.00
74.6	8.1	7.8	152	0.70	9.90	12.7	103	1.80	0.47
100	8.1	7.8	126	0.64	10.11	10.4	85	1.70	0.14

TABLE 12 (continued)

I mole/l x 10 ³	EC mmhos/cm	O.P. atm	$\frac{1}{2}$ PCa- PNa	$\frac{1}{2}$ PMg- PNa	PCa- PMg	PK- $\frac{1}{2}$ P (Ca+Mg)	PNa- $\frac{1}{2}$ P (Ca+Mg)	PKsp for CaSO ₄ ·2H ₂ O mole/l	
								PK-PNa	PKsp
136	7.50	2.70	0.312	0.165	0.295	1.79	-0.076	1.87	4.21
91	4.76	1.71	0.173	0.006	0.334	1.80	0.068	1.73	4.50
84	4.60	1.66	0.139	-0.010	0.298	1.81	0.097	1.71	4.54
78	4.10	1.48	0.114	-0.025	0.277	1.83	0.117	1.71	4.57
66	3.50	1.26	0.064	-0.059	0.266	1.85	0.157	1.70	4.69
31	2.00	0.72	-0.024	-0.167	0.285	1.85	0.252	1.60	5.54
828	33.0	11.9	0.855	0.380	0.949	2.29	-0.357	2.55	2.99
471	18.6	6.70	0.455	0.219	0.472	2.28	-0.256	2.43	2.99
421	16.8	6.05	0.378	0.180	0.396	2.32	-0.107	2.42	3.00
407	16.4	5.98	0.355	0.170	0.369	2.31	-0.093	2.41	3.00
291	11.5	4.14	0.152	0.029	0.246	2.35	0.068	2.29	3.13
210	8.35	3.44	-0.021	-0.068	0.093	2.36	0.196	2.17	3.27
1519	60.0	21.6	1.241	0.490	1.503	2.49	-0.484	2.97	2.98
577	22.5	8.53	0.633	0.385	0.496	2.38	-0.325	2.71	2.97
443	18.0	6.23	0.442	0.299	0.286	2.37	-0.209	2.58	2.99
426	16.9	6.08	0.405	0.280	0.250	2.40	-0.183	2.58	2.98
321	12.8	4.62	0.153	0.090	0.126	2.42	0.031	2.39	2.99
249	10.0	3.60	-0.015	-0.057	0.085	2.45	0.188	2.26	3.10
1474	55.0	19.8	1.212	0.460	1.50	2.45	-0.454	2.90	2.98
582	24.0	6.84	0.606	0.330	0.551	2.27	-0.276	2.54	3.03
454	16.2	6.19	0.469	0.290	0.357	2.29	-0.211	2.50	3.02

TABLE 13

Change of Ion Concentrations, Cation Activity Ratios and Other Properties
of Malmo Soil Equilibrium Solutions with Change in Moisture Content

Moisture (%)	pH (Suspension)	pH (filtrate)	Concentrations of ions mole/l x 10 ³						
			Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	SO ₄ ⁻⁻	HCO ₃ ⁻	Cl ⁻
Ap (0 - 4½")									
14.6	5.9	6.0	2.54	3.85	1.88	2.03	3.98	4.00	1.82
26.6	5.9	6.2	2.41	3.53	1.70	1.81	3.08	3.95	1.69
34.5	5.9	6.2	2.30	3.32	1.57	1.67	2.98	3.77	1.56
42.3	5.9	6.2	2.21	2.80	1.45	1.53	2.50	3.59	1.41
79.1	6.1	6.4	1.79	1.78	0.85	0.85	1.53	3.33	0.67
100	6.1	6.7	1.58	1.25	0.55	0.51	1.25	2.35	0.30
Ah & Ahe (4½ - 12")									
6.4	6.2	6.2	2.45	2.59	0.59	0.59	1.27	4.00	0.85
22.0	6.2	6.2	2.41	2.33	0.54	0.57	1.28	3.79	0.82
26.6	6.2	6.2	2.40	2.29	0.53	0.57	1.28	3.56	0.79
31.2	6.2	6.4	2.39	2.18	0.52	0.57	1.28	3.26	0.75
47.3	6.3	6.3	2.34	1.95	0.48	0.55	1.26	3.00	0.66
100	6.4	6.4	2.15	1.66	0.37	0.52	1.18	2.60	0.31
Bt ₁ (12 - 26")									
4.5	7.0	7.7	10.03	2.35	3.48	2.29	6.79	8.86	0.87
22.2	7.0	7.7	9.25	2.23	3.05	2.00	5.50	8.98	0.74
27.1	7.0	7.7	9.00	2.20	2.87	1.88	5.15	8.55	0.68
32.1	7.0	7.8	8.72	2.16	2.77	1.75	4.98	8.33	0.63
56.7	7.0	7.8	7.88	1.92	2.04	1.13	3.75	8.25	0.55
100	7.1	7.6	6.55	1.43	1.17	0.37	2.38	6.32	0.23
Bt ₂ (26 - 60")									
2.4	7.2	7.7	17.1	0.39	5.25	5.25	18.0	3.65	0.42
11.6	7.1	7.7	16.7	0.36	5.17	5.01	17.2	3.49	0.39
17.7	7.1	7.6	16.5	0.33	5.09	4.92	16.9	3.34	0.39
23.7	7.1	7.6	16.3	0.31	4.81	4.63	16.3	3.22	0.37
40.1	7.2	7.6	15.2	0.26	3.99	3.60	13.3	3.00	0.31
100	7.1	7.7	12.9	0.26	1.25	0.79	3.96	2.26	0.14

TABLE 13 (continued)

I mole/l x 10 ³	EC mmhos/cm	O.P. atm	$\frac{1}{2}\text{pCa}-\text{pNa}$	$\frac{1}{2}\text{pMg}-\text{pNa}$	pCa-pMg	$\text{pK}-\frac{1}{2}\text{p}$ (Ca+Mg)	$\text{pNa}-\frac{1}{2}\text{p}$ (Ca+Mg)	pK-pNa	pKsp for CaSO ₄ .2H ₂ O mole/l
21.9	1.60	0.58	-1.18	-1.21	0.050	1.17	1.34	-0.177	5.59
18.0	1.42	0.51	-1.18	-1.21	0.043	1.18	1.34	-0.163	5.72
17.9	1.35	0.49	-1.18	-1.21	0.041	1.19	1.35	-0.156	5.76
16.0	1.15	0.41	-1.18	-1.21	0.036	1.25	1.35	-0.100	5.85
10.3	0.76	0.27	-1.17	-1.18	0.009	1.33	1.32	0.005	6.23
7.36	0.55	0.20	-1.14	-1.12	-0.025	1.38	1.28	0.103	6.46
9.85	0.80	0.29	-0.957	-0.961	0.009	1.08	1.11	-0.031	6.46
9.46	0.76	0.27	-0.945	-0.961	0.033	1.12	1.10	0.017	6.49
9.28	0.73	0.26	-0.944	-0.964	0.040	1.13	1.10	0.022	6.50
9.00	0.70	0.25	-0.942	-0.966	0.048	1.15	1.11	0.040	6.50
8.56	0.69	0.25	-0.934	-0.967	0.067	1.18	1.10	0.080	6.54
7.50	0.58	0.21	-0.916	-0.993	0.155	1.22	1.11	0.114	6.66
36.2	2.60	0.94	-0.697	-0.617	-0.159	1.46	0.812	0.648	5.19
31.7	2.35	0.85	-0.717	-0.636	-0.162	1.46	0.832	0.623	5.31
30.0	2.20	0.79	-0.718	-0.636	-0.164	1.45	0.832	0.616	5.36
28.9	2.15	0.77	-0.724	-0.632	-0.183	1.44	0.834	0.606	5.38
23.1	1.70	0.61	-0.705	-0.585	-0.240	1.42	0.805	0.617	5.59
15.1	1.10	0.40	-0.671	-0.427	-0.488	1.40	0.734	0.661	5.96
67.8	4.05	1.46	-0.556	-0.574	0.036	2.37	0.715	1.65	4.71
65.3	3.90	1.40	-0.563	-0.574	0.021	2.39	0.719	1.68	4.73
64.1	3.80	1.37	-0.566	-0.575	0.019	2.43	0.721	1.71	4.74
61.5	3.66	1.22	-0.561	-0.569	0.017	2.44	0.715	1.73	4.78
51.1	3.00	1.08	-0.552	-0.544	-0.016	2.47	0.698	1.77	4.91
20.2	1.20	0.43	-0.387	-0.296	-0.183	2.29	0.498	1.70	5.76

TABLE 1.1-1

Char
of

isture
(%)

14.6
26.6
34.5
42.3
79.1
100

6.4
22.0
26.6
31.2
47.3
100

4.5
22.2
27.1
32.1
56.7
100

2.4
11.6
17.7
23.7
40.1
100

Sample	Temperature, °C	Time, min	Weight, g	Volume, ml	Density, g/ml	Moisture, %
1	100	10	10.0	10.0	1.00	14.6
2	100	20	10.0	10.0	1.00	26.6
3	100	30	10.0	10.0	1.00	34.5
4	100	40	10.0	10.0	1.00	42.3
5	100	50	10.0	10.0	1.00	79.1
6	100	60	10.0	10.0	1.00	100
7	100	70	10.0	10.0	1.00	6.4
8	100	80	10.0	10.0	1.00	22.0
9	100	90	10.0	10.0	1.00	26.6
10	100	100	10.0	10.0	1.00	31.2
11	100	110	10.0	10.0	1.00	47.3
12	100	120	10.0	10.0	1.00	100
13	100	130	10.0	10.0	1.00	4.5
14	100	140	10.0	10.0	1.00	22.2
15	100	150	10.0	10.0	1.00	27.1
16	100	160	10.0	10.0	1.00	32.1
17	100	170	10.0	10.0	1.00	56.7
18	100	180	10.0	10.0	1.00	100
19	100	190	10.0	10.0	1.00	2.4
20	100	200	10.0	10.0	1.00	11.6
21	100	210	10.0	10.0	1.00	17.7
22	100	220	10.0	10.0	1.00	23.7
23	100	230	10.0	10.0	1.00	40.1
24	100	240	10.0	10.0	1.00	100

was present even at the 100 per cent moisture equilibrium level. Because of the relatively great ability of calcium to replace exchangeable sodium, however, it is realized that transfer of calcium from the gypsum to the solution and thence to the exchange complex would increase on dilution. This reaction in turn would also result in further solubilization of gypsum. In view of the foregoing the amount of solid gypsum in the soils can not be readily predicted by the equilibrium solutions. This aspect will be considered later.

Variation in Ionic Strength with Change in Soil Moisture: The ionic strengths (I) of the equilibrium solutions range from 31 to 1519 mmols/l for the Duagh and 7.36 to 67.8 for the Malmo soil (Tables 12 and 13). The effect of moisture variation on ionic strength is also shown graphically in Figs. 9 and 10. In the sub-surface horizons of the Duagh soil the ionic strength increased gradually as the moisture decreased from 100 to 30 per cent followed by an abrupt increase with further drying (Fig. 9). In the surface Ap horizon it follows a similar pattern as observed for the Malmo soil, that is, the ionic strength of the equilibrium solutions increased gradually with decrease in moisture over the entire range studied (Fig. 10). Moss (1963a), in a similar study on non-saline soils, found a sharp increase in concentration of ions with decreasing moisture in a range usually encountered under field conditions. The decrease in concentrations becomes less rapid with dilution beyond the field range of moisture content. In the present study ionic strengths of equilibrium solutions were used rather than concentrations as the former were considered a more useful criterion of the behaviour of the solution than

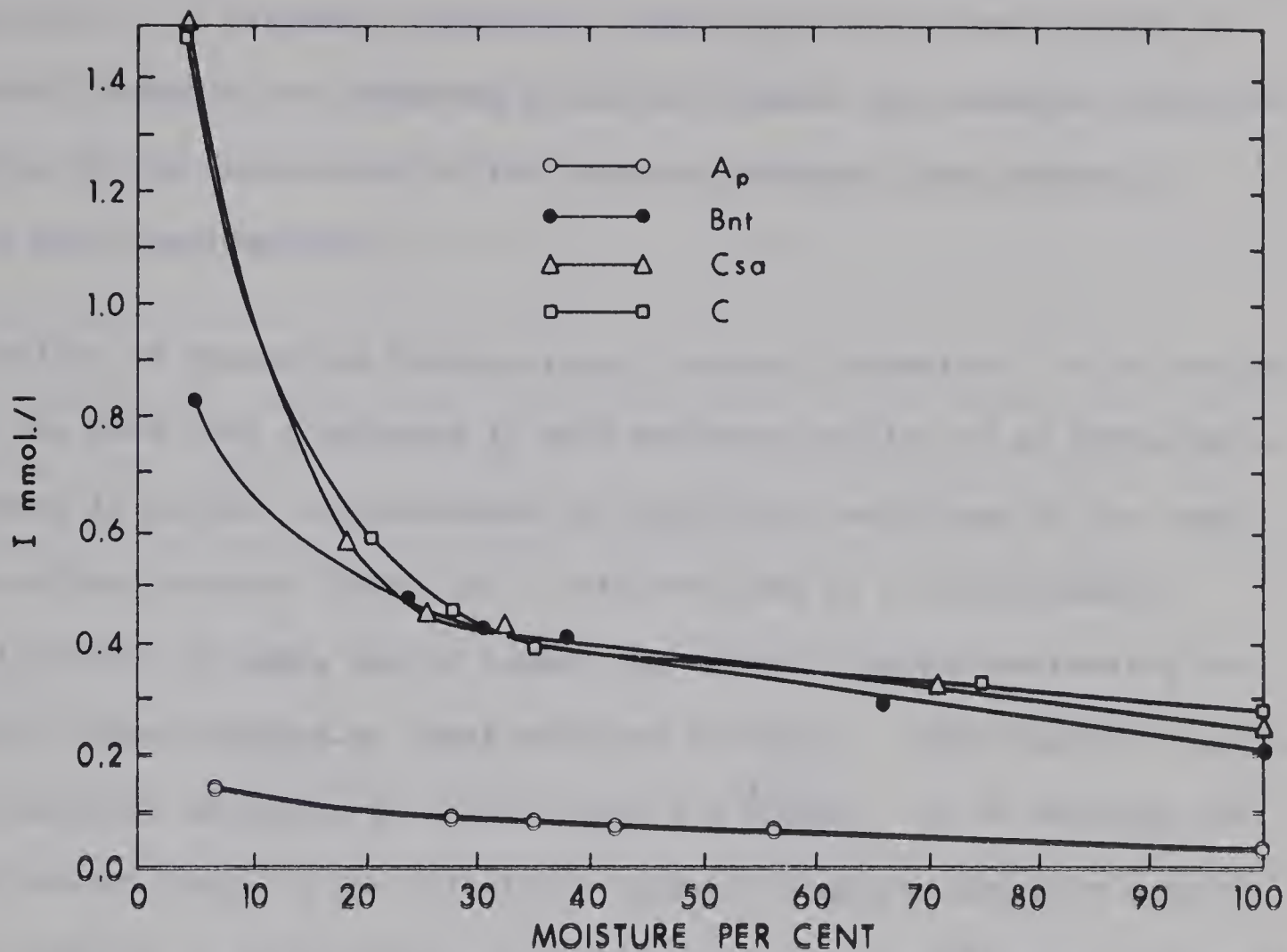


Fig. 9. Change in ionic strength of equilibrium solution with change in moisture content in the Duagh silt loam soil

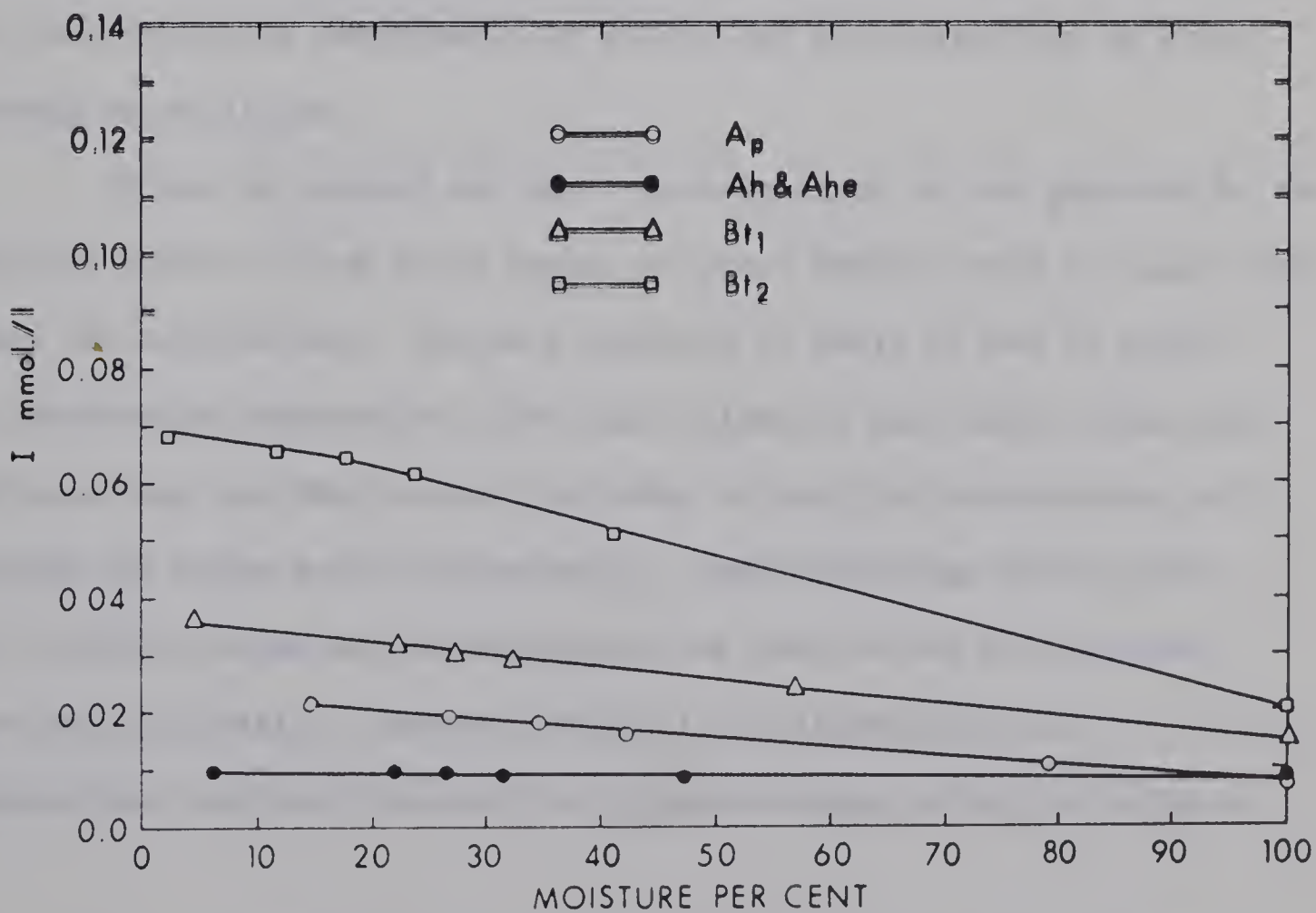


Fig. 10. Change in ionic strength of equilibrium solutions with change in moisture content in the Malmo silt loam soil

the latter. It has been pointed out previously that ionic strength is a useful property for comparing solutions because the specific electrical effects of the interaction of the variously charged ions present are taken into consideration.

Solubility of Gypsum and Undissociated Ion-pair Formation: It is obvious from the data that a decrease in soil moisture results in an appreciable increase in sulfate concentration in equilibrium solutions of the Duagh sub-surface horizons (Table 12). This resulted in a corresponding precipitation of CaSO_4 due to common ion effects thereby decreasing the calcium concentrations at lower moisture contents. Unfortunately, reports on solubility of gypsum in saline soils are scarce. It is realized that calculations based on the solubility product principle are only possible if a procedure is available for obtaining activity coefficients of the species involved in equilibrium solutions otherwise it is necessary to study such solutions experimentally before any conclusion can be drawn regarding solubilities.

It may be pointed out that the solubility is not governed by the solubility product alone and a number of other factors must be taken into account in calculations. The data reported in Table 12 and 13 reveal some interesting information. The last column of each Table shows the calculated PKsp and pKsp values for CaSO_4 in equilibrium solutions of the Duagh and Malmo soils respectively. Some misgivings may be felt about the PKsp values as concentrations are used in the calculations rather than activities. However, there is no alternative and concentrations are used in order to illustrate some solubility effects

qualitatively. In the case of CaSO_4 , the theoretical Ksp value is 1.95×10^{-4} and thus the corresponding pKsp value will be equal to 3.71. It is noted that the values of pKsp for the Malmo and PKsp for the Duagh surface soils were greater than 3.71 (Tables 12 and 13). However, the PKsp values were lower than this for the sub-surface horizons of the latter soil. These compare well with some of the values calculated from the data reported in literature for soils containing salts. These references were selected at random and PKsp values obtained were as follows:

Kelley (1951) p. 106-107

Sample #	PKsp
6 (Alkali soil)	2.89
34 "	2.39
46 "	2.47

Bowser et al (1962)

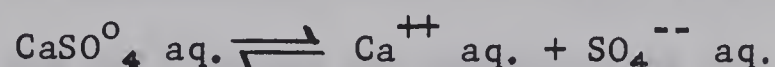
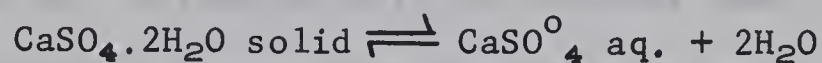
Soil	PKsp
Wetaskiwin silt loam Bts	2.88

Arshad and Pawluk (1966)

Soil	PKsp
Black solonetz Cs	3.20

The foregoing data indicate an enhanced solubility of calcium sulfate and Davies (1962) attributed this to ion-pair formation. Butler (1964) has also pointed out that ion-pair formation may occur in salts such as calcium sulfate and this would tend to increase the solubility over the value calculated from the solubility product alone. The results of Moreno and Osborn (1963) and Paul et al (1966) also demonstrate the

presence of undissociated calcium sulfate ion-pair (CaSO_4^0) in soils containing gypsum. The former authors have shown that complex species (CaSO_4^0) constituted from 33 to 38 per cent of the total calcium in solution. In view of the foregoing the following equilibrium can be postulated:



The studies carried out by Garrels and Thompson (1962) are also of particular interest. They pointed out that interaction of major dissolved species in natural waters less concentrated ($I = 0.01$) than sea water ($I = 0.7$) is relatively slight. However, in the latter case, the ionic strength is sufficiently high to have interaction between ions that markedly modify the thermodynamic properties. On the basis of the above paper and the discussion presented by Harned and Owen (1958) and Davies (1962), it is the author's opinion that a modification of the concept of 'complete' ionization of the major components dissolved in solutions seems to be unnecessary for most purposes at ionic strengths below about 0.05. However, at higher values, increasing interactions takes place and a large percentage of the anions can be considered to form ion-pairs with cations. Considering the fact that sulfate is the dominant soluble anion in the Duagh soil and following the assumption of Garrels and Thompson (1962), it is postulated that the important ion-pairs in the equilibrium solutions of the sub-surface horizons of the Duagh soil are CaSO_4^0 , MgSO_4^0 , NaSO_4^- , and KSO_4^- . Thus, as pointed out by Garrels and

Thompson (1962), the analytical value given for SO_4^{--} concentration, which can be designated as $^m\text{SO}_4^{--}\text{total}$ can be equated to the sum of the various species containing sulfate, i.e. $^m\text{SO}_4^{--}\text{total} = ^m\text{CaSO}_4^0 + ^m\text{MgSO}_4^0 + ^m\text{NaSO}_4^- + ^m\text{KSO}_4^- + ^m\text{SO}_4^{--}\text{free}$.

Therefore, the ion-pair formation of dissolved species in concentrated soil solutions will distinguish them from the dilute solutions. The complication in determining these ion-pairs in soil solutions seems overwhelming and the only method for dealing with the problem appears, as has been always done in the past, to make an assumption that cations are not significantly complexed. Nevertheless, the foregoing speculation warrants further research.

Variation in IR_0 Values with Change in Moisture: Tables 12 and 13 show the changes in various cation concentration ratios and activity ratios (hereafter both called IR_0 values) in equilibrium solutions with change in moisture content of soils. The patterns of IR_0 values for various ion-pairs with changing moisture were nearly identical for the sub-surface horizons within each profile. Therefore, only one sub-surface horizon within each profile and the surface Ap horizons were used for graphic representation (Figs. 11, 12, 13 and 14).

K-(Ca + Mg) expression: The IR_0 values for K-(Ca + Mg) expressions were almost constant over the entire moisture range within each horizon of the Duagh and the Malmo soils (Tables 12 and 13; Figs. 11, 12, 13 and 14). This indicates that the release of potassium with respect to calcium and magnesium was sufficient at all moisture contents to maintain constant IR_0 values. Moss (1963a) found that

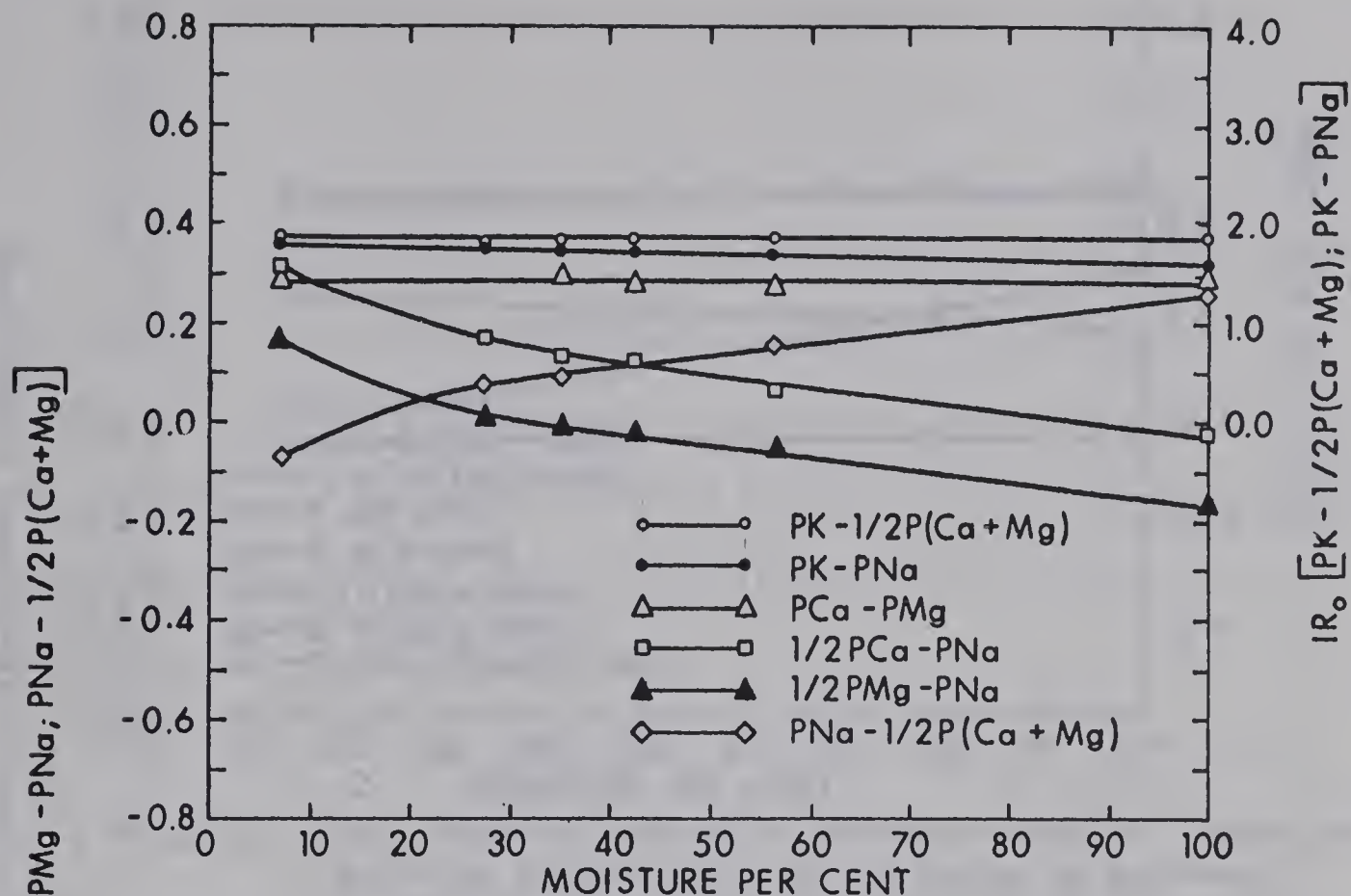


Fig. 11. The effect of change in moisture content on the cation concentration ratios (IR_o) of the Duagh Ap horizon equilibrium solutions

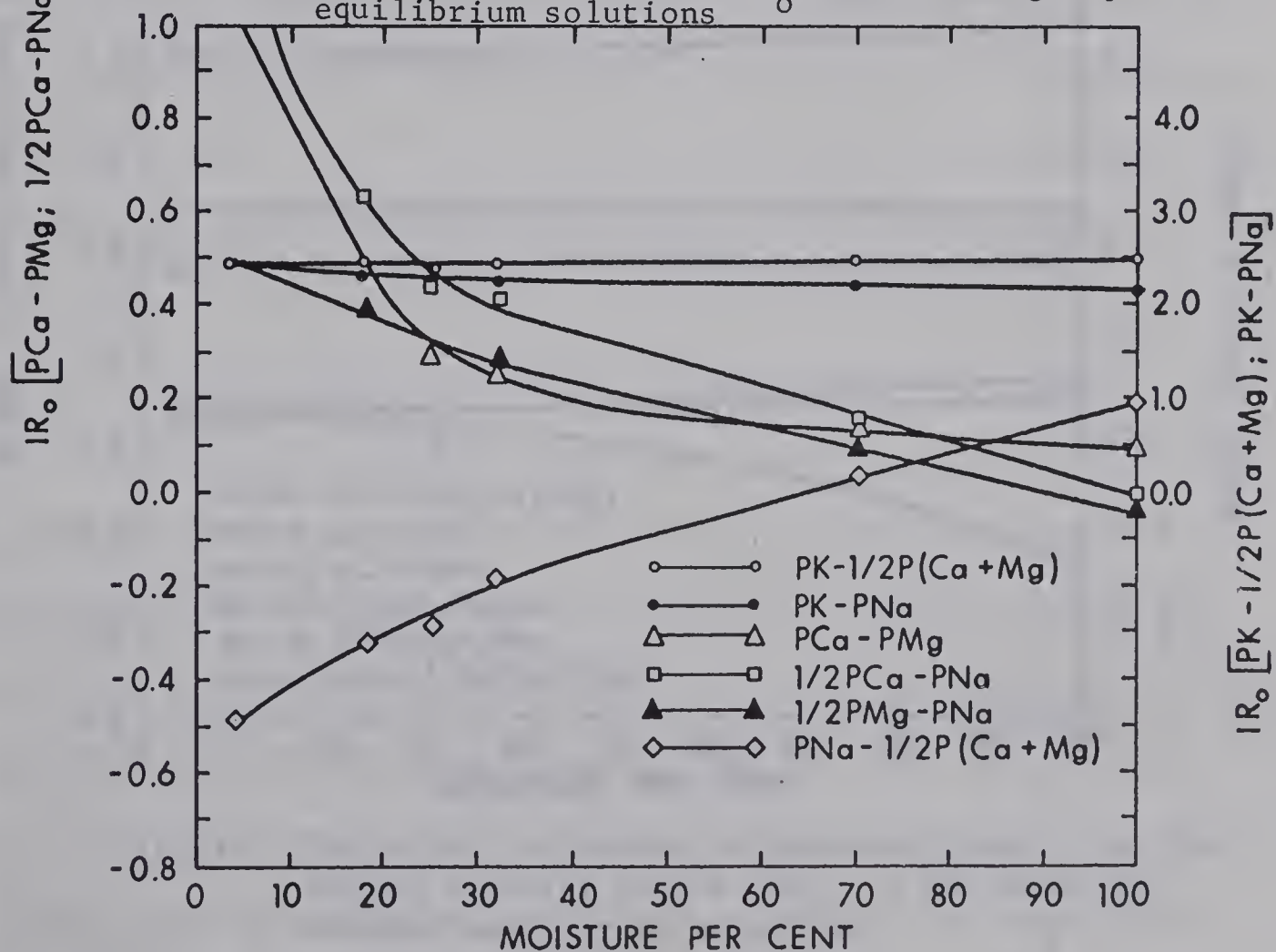


Fig. 12. The effect of change in moisture content on the cation concentration ratios (IR_o) of the Duagh Csa horizon equilibrium solutions

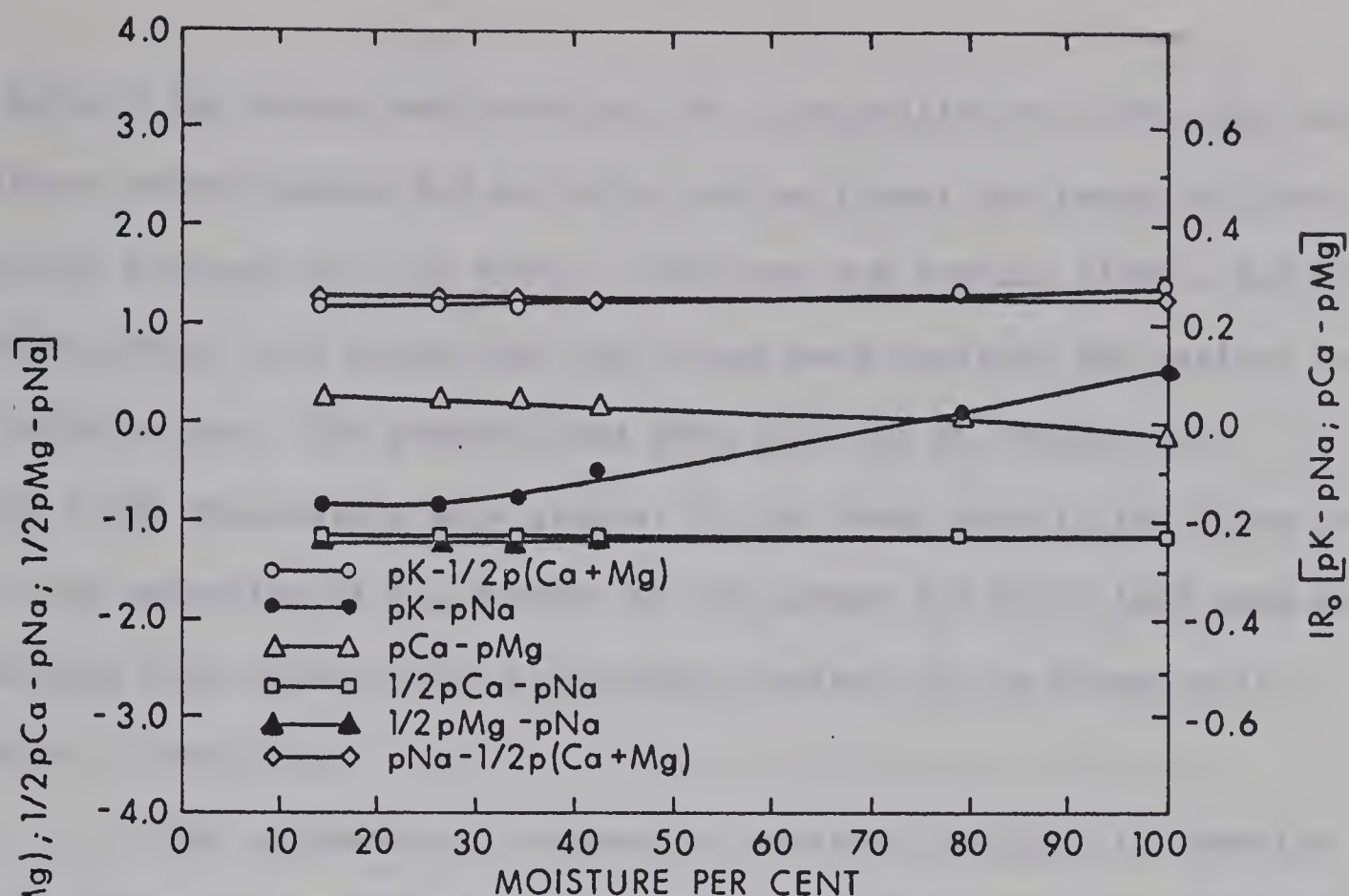


Fig. 13. The effect of change in moisture content of the cation activity ratios (IR_o) of the Malmo Ap horizon equilibrium solutions

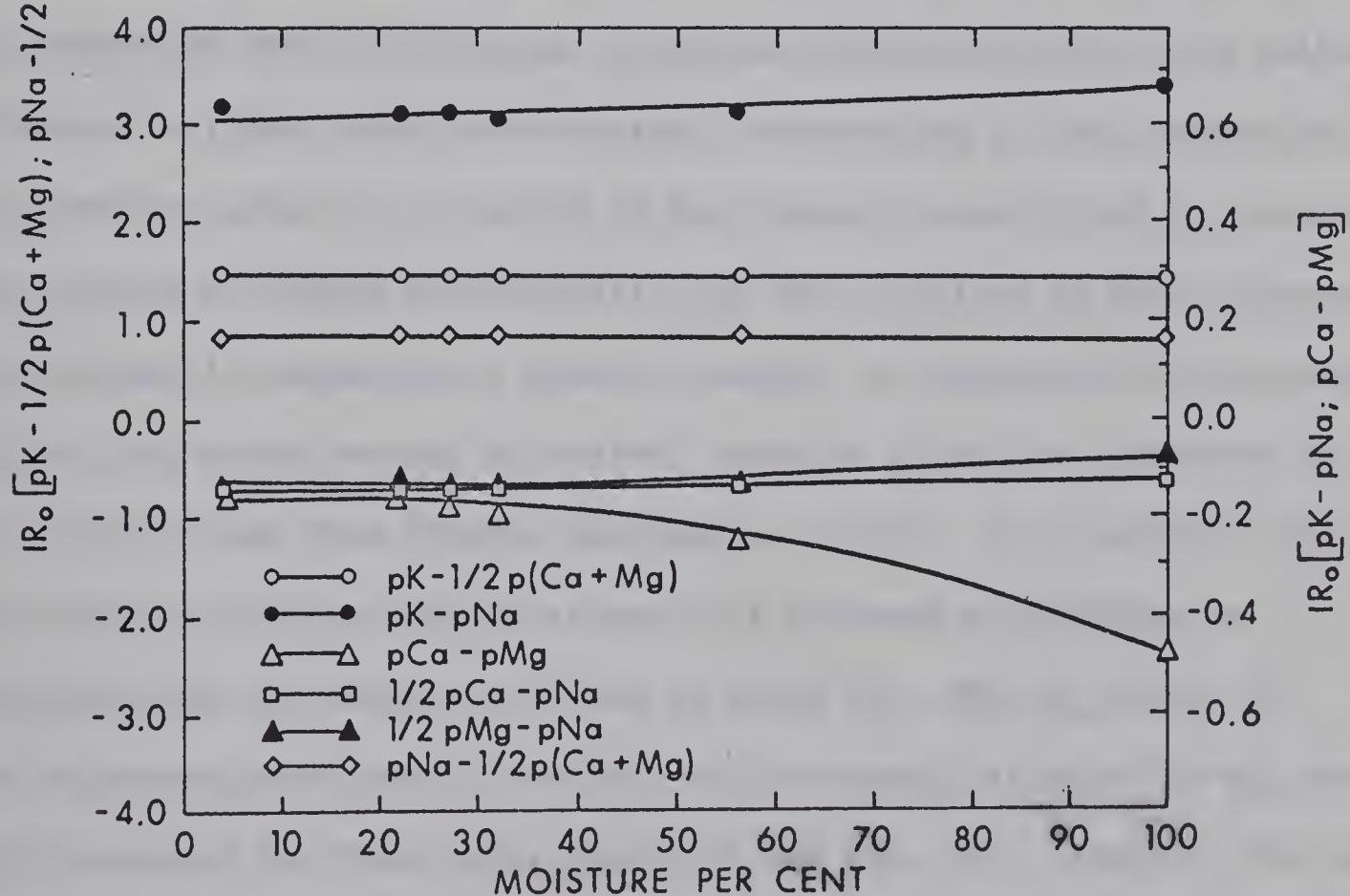


Fig. 14. The effect of change in moisture content on the cation activity ratios (IR_o) of the Malmo Bt₁ horizon equilibrium solutions

$pK-\frac{1}{2}p(Ca + Mg)$ values were constant for a non-saline soil over the entire moisture range studied for one soil, but only over the range of field moisture contents for two others. Matthews and Beckett (1962), and Moss (1963b; 1964a) also found that the values were constant for various soil solution ratios. The present data show that the IR_0 values for $K-(Ca + Mg)$ expressions were greater in the Duagh than in the Malmo soil with the exception of Bt_2 horizon of the latter for which they were almost identical with those of the sub-surface horizon of the former soil (Tables 12 and 13).

K-Na expression: Increase in moisture resulted in lowering of IR_0 values in equilibrium solutions for the K-Na expression in the Duagh soil, although the decrease was not marked (Table 12; Figs. 11 and 12). This indicates that on dilution, potassium increased relative to sodium. Reitemeier's (1946) data are especially interesting in this connection. The principal effect of dilution on the Reagan loam soil was to increase the solution of gypsum substantially and this resulted in the replacement of exchangeable magnesium in greatest amount, of potassium in considerable amounts, and minor amounts of sodium. Similar effect was observed for Fort Collins loam from Wyoming (Reitemeier, 1946). It is obvious that under these conditions $pK-pNa$ values will decrease on dilution in agreement with the results reported in Table 12. The IR_0 values for K-Na expression were nearly constant with moisture variation in Bt_1 and Bt_2 horizons of the Malmo soil (Table 13 and Fig. 14). However, the values increased rather markedly with increasing moisture in Ap, Ah & Ahe horizons (Table 13, Fig. 13). Dilution leads to a release of exchangeable potassium and sodium into the intermicellar solution. It is evident that

potassium tends to be released in lower amounts relative to sodium resulting in higher values of $pK-pNa$. It will be noted that the IR_0 values for K-Na expressions were very much larger in the Duagh than those in the Malmo soil (Tables 12 and 13). However, the values in the Bt_2 horizon of Malmo were nearly the same as in the Ap horizon of the Duagh soil.

Ca-Mg expression: The IR_0 values for Ca-Mg expression were virtually constant over the entire moisture range of Ap horizon of the Duagh soil (Table 12; Fig. 11). Similar results for a non-saline soil have also been reported elsewhere (Moss, 1964a). However, in the sub-surface horizons of the Duagh soil the values decreased abruptly as the moisture increased over the range up to about 30 per cent but less markedly over the higher moisture range (Table 12; Fig. 12). This is attributed to the dissolution of gypsum with increase in moisture. Over the entire moisture range the IR_0 values for the Ca-Mg expression for the Malmo Ap horizon decreased gradually with increase in moisture (Table 13; Fig. 13), whilst an increase was noted for Ah & Ahe horizons (Table 13). On the other hand, an increase in moisture up to about 50 per cent in Bt_1 and Bt_2 horizons of the Malmo soil, resulted in a gradual decrease of IR_0 values followed by a rapid decrease with further increase in moisture (Table 13; Fig. 14). It is evident that concentration of magnesium decreased relative to calcium, to a greater extent at the higher moisture contents.

Ca-Na expression: The values of $\frac{1}{2}PCa-PNa$ decreased with increasing moisture content in the Duagh soil (Table 12) particularly

in the sub-surface horizons over the lower moisture range (Table 12; Fig. 12). That is, calcium concentration in equilibrium solutions increased markedly relative to sodium; however, with further increase in moisture proportionally more solution calcium was adsorbed on the exchange surface at the expense of sodium as predicted by the dilution law. This obviously resulted in a more gradual decrease of IR_0 values at the higher moisture range. The values were nearly constant with variation in moisture in Ap and Ah & Ahe horizons of the Malmo soil (Table 12; Fig. 13). However, a slight increase was noted at the higher moisture range (saturation to 100 per cent) in Bt_1 and Bt_2 horizons (Table 13; Fig. 14). This is again attributed to the 'dilution effect'. The data show that the values were much greater in the Duagh than those in the Malmo soils (Tables 12 and 13).

Mg-Na expression: The variation in IR_0 values for Mg-Na expressions in the Duagh soil were somewhat similar to those found for Ca-Na, however, the changes were not nearly as marked over the low moisture range (Table 12; Figs. 11 and 12). It appears that an increase in moisture resulted in an increase of magnesium in amounts greater than sodium and this is in agreement with the results reported by Reitemeier (1946) for soils containing gypsum. The values of $\frac{1}{2}pMg-pNa$ were nearly constant with moisture variation in Ah & Ahe horizons of the Malmo soil (Table 13). However, over the higher moisture range a slight increase was noted in the Ap, Bt_1 and Bt_2 horizons due to dilution effect (Table 12; Figs. 13 and 14). In all horizons of the Duagh soil the IR_0 values for Mg-Na expression were greater than found in Malmo.

Na-(Ca + Mg) expression: Calcium and magnesium were pooled together and the IR_0 values are shown in Table 12 and 13 and Figs. 11 to 14. The values increased with increase in moisture in the Duagh soil and the effect was more marked at lower moisture range (Table 12 and Figs. 11 and 12). Probably the same factors are operative in this case as were discussed previously for Ca-Na and Mg-Na expressions thereby causing an increase in $pNa-\frac{1}{2}p(Ca + Mg)$ values with increase in moisture content. The values of $pNa-\frac{1}{2}p(Ca + Mg)$ were nearly constant over the entire moisture range in the Malmo Ap, Ah & Ahe horizons (Table 13; Fig. 13). However, at the higher moisture range the values for Malmo Bt₁ and Bt₂ decreased slightly with increase in moisture content (Table 13; Fig. 14). When the moisture content of a soil is increased one may expect to increase exchange between calcium and magnesium in solution and sodium on the exchange surface purely by the 'dilution effect' so that $pNa-\frac{1}{2}p(Ca + Mg)$ in solution would decrease. The data show that the values were much smaller in Duagh than in Malmo soil.

The foregoing discussion clearly distinguishes the equilibrium solutions at various moisture contents of the Duagh soil from those of the Malmo. Firstly, it is obvious that variation in moisture resulted in markedly different patterns of IR_0 values in the two soils, and secondly, the magnitude of IR_0 values in equilibrium solutions were different. In view of the fact that the Malmo soil is more productive than the Duagh, it is probably logical to postulate that the equilibrium solutions and various IR_0 values obtained for the former soil are more favourable for plant growth than the latter. However, this can only be

confirmed by growing various crops in these solutions. This aspect of the problem is considered in a later section.

Equilibrium Status and Ratio Law: The constancy of $pK - \frac{1}{2}p(Ca + Mg)$ over a range of moisture would indicate an undisturbed equilibrium (Moss, 1963a). It is noted that equilibrium remained relatively undisturbed over the entire moisture range studied in both soils as there were no appreciable changes in IR_o values for $K - (Ca + Mg)$ expressions (Tables 12 and 13; Figs. 11 and 14). Equilibrium remained constant for most ion-pairs in the Malmo (Table 13) but not for the Duagh soil (Table 12). It is postulated that in the Duagh soil equilibrium was attained at every moisture content studied, but its position or status was changed with change in moisture. It is therefore important to realise that equilibrium may remain undisturbed over the moisture range with respect to one ion-pair, however, its position may be changed with respect to others.

The constancy of various ion-pairs over a range of ionic strength is the criterion used by several workers to confirm the 'Ratio Law' (Schofield and Taylor, 1955a; 1955b; Taylor, 1958; Salmon, 1962; 1964a; Moss, 1963a; 1963b; 1963c; Moss and Hodnett, 1963; Khasawneh and Adams, 1965). It has been shown that the values of $pK - \frac{1}{2}p(Ca + Mg)$ in dilute solutions were largely independent of total electrolyte concentration (Beckett, 1964a; Salmon, 1964b). However, Taylor (1958) found that of the four soils examined, only two gave values of $pK - \frac{1}{2}p(Ca + Mg)$ which were independent of the electrolyte concentrations. In the other two soils, there was a steady fall in the values with increasing electrolyte concentration. Also, Moss (1964b) reported that in some soils $pK - \frac{1}{2}p(Ca + Mg)$

values decreased rapidly with increasing ionic strength over the lower ionic strength range, the decrease becoming less rapid with a further increase in ionic strength. Similar studies by Matthews and Beckett (1962) and Salmon (1962) suggest that the activity ratios for the ion-pair $K-(Ca + Mg)$ in equilibrium solutions were independent up to electrolyte concentrations of 0.06 M and 0.02 M respectively. Schofield and Taylor (1955) have pointed out that the concentration above which deviations from linearity occurred varied with different cations. Furthermore, the effect of anion such as sulfate will be more pronounced than chloride (Schofield and Taylor, 1955). In view of the foregoing, the data presented in Tables 12 and 13 show that the 'Ratio Law' was adequately confirmed for most of the ion-pairs for the Malmo soil. However, in general the data were not consistent with the Law in the Duagh soil presumably because of the high ionic strength of equilibrium solutions.

Sulfate Concentration and IR_o Values: Since sulfate is the dominant soluble anion in the Duagh soil, it was deemed desirable to examine the effects of sulfate concentration in equilibrium solutions on the IR_o values for various ion-pairs. Correlation coefficients (r) and coefficient of determination (r^2) derived for Duagh soil are shown in Table 14. The PSO_4 values in equilibrium solutions were significantly correlated with all the ratios studied. A positive correlation was noted only for ion-pair $Na-(Ca + Mg)$ suggesting that an increase in sulfate concentration would result in a decrease of the IR_o values. It is noteworthy that the highest correlation coefficient was obtained for PK-PNa whilst it was least,

TABLE 14

Statistical Data Pertaining to the Relation Between PSO_4
and IR_O Values for Various Ion-pairs in Duagh Soil

IR_O	r	$r^2 \times 100$
$\text{PK}-\frac{1}{2}\text{P} \text{ (Ca + Mg)}$	-0.823	68
$\text{PK}-\text{PNa}$	-0.975	95
$\text{PCa}-\text{PMg}$	-0.525	28
$\frac{1}{2}\text{PCa}-\text{PNa}$	-0.806	65
$\frac{1}{2}\text{PMg}-\text{PNa}$	-0.886	79
$\text{PNa}-\frac{1}{2}\text{P} \text{ (Ca + Mg)}$	+0.867	75

$r = 0.404$ at $P = 0.05$

although significant, for PCa-PMg. It may be pointed out, however, that significance of a correlation coefficient does not justify use of one variable as a satisfactory predictor of another. It is clear from the corresponding values for the coefficient of determination, that, at best, only 28 per cent of variance in PSO_4 is associated with concomitant variance in PCa-PMg values. On the other hand it is obvious that the variation of PSO_4 can explain as much as 95 per cent of the variance in PK-PNa. For other ion pairs the coefficient of determination values ranged from 65 to 79 per cent (Table 14). Thus it is evident that the variation in sulfate concentrations in equilibrium solutions will have a significant effect on IR_0 values for various ion pairs. The effect will be more marked on PK-PNa as compared to other ratios. It is pertinent to recall (Chapter 3) that when ground water table rises, sulfate accumulation was greater near the surface than at lower depths in Duagh soil. In such cases it is obvious that various ion ratios will be changed significantly and this might have an important bearing on plant growth.

Electrical Conductivity: The measurements of electrical conductivity of soil solutions is recognized as giving a fair indication of total soil salinity. The conductivity of saturation extracts is recommended as a general method for appraising soil salinity in relation to plant growth (U.S. Salinity Laboratory Staff, 1954). The data reported in Tables 12 and 13 reveal that electrical conductivity of the equilibrium solutions increased with decrease in moisture content of the soils studied as would be anticipated. The values were greater in the field moisture range than those measured at saturation percentage. Therefore, it would be more

reliable to appraise salinity by using measurements of extracts of the soil solution in the moisture range normally encountered under field conditions. The data suggest a linear increase of electrical conductivity with ionic strength (Tables 12 and 13) and a high correlation exists. The correlation coefficients being 0.988 and 0.969 for Duagh and Malmo soils respectively. Ponnampereuma et al (1966) found that the ionic strength (moles/l), numerically was approximately 16 times the specific conductance (mhos cm^{-1}) of the solutions of flooded soils. A high degree of correlation between electrical conductivity of soil solutions and total soluble cations (Campbell et al, 1948; U.S. Salinity Laboratory Staff, 1954; Agarwal and Yadave, 1955) and total soluble salts (Mondal and Jain, 1966) has been reported in the literature.

Osmotic Pressure: Osmotic pressure of the soil solutions has a marked influence on the rate of water uptake and growth of plants in saline soils and it can be estimated from electrical conductivity values by the relationship, $\text{O.P.} = 0.36 \text{ EC}$, when electrical conductivity is expressed in millimhos per centimeter (U.S. Salinity Laboratory Staff, 1954). The osmotic pressure for equilibrium solutions calculated by this relationship are reported in Tables 12 and 13. The decrease in soil moisture resulted in increased osmotic pressure of the equilibrium solutions. The values ranged from 0.720 to 21.6 for the Duagh and 0.20 to 1.46 atm for the Malmo soil. According to Russell (1961) the osmotic pressure of solutions of normal leached agricultural soils varies from 0.2 to 1 atm. Even at the wilting-point the soil solutions is very dilute and has the value far lower than the 10 to 20 atm of root sap. However, the osmotic pressure of soil

solutions of arid and semi-arid soils is no longer negligible, but may become high enough to limit crop growth. Crops cannot make appreciable growth in a solution having an osmotic pressure of 10 atm. Furthermore, he pointed out that crop growth may be reduced in proportion as the osmotic pressure rises from 2 to about 10 atm. In view of the foregoing it appears that in the field moisture range the very high osmotic pressure of equilibrium solutions might also be one of the contributory factors for low productivity of the Duagh soil (Table 12). The values were lower in the Malmo soil than the suggested upper limits and plant growth should not be adversely affected (Table 13).

pH of Filtrates and Suspensions: There appears to be no appreciable change in pH of suspensions or filtrates (equilibrium solutions) for either soil with change in moisture content (Tables 12 and 13). The filtrates of Ap and Bnt horizons of the Duagh soil and all horizons of the Malmo soil showed a greater pH than those of suspensions. This is obviously due to the 'suspension effect' (Coleman et al, 1950). However, a somewhat reverse trend, although insignificant, was observed for Csa and C horizons of the Duagh soil (Table 12). According to Wiklander (1964) many soils exhibit an increase in pH of soil suspension on addition of neutral salts, for example, sodium sulfate. Since sodium sulfate was the dominant salt present in the Duagh soil, it seems probable that due to its high concentration the pH of suspensions were higher than those of the corresponding filtrates. Also the presence of an electrolyte reduces the suspension on effect mentioned earlier.

Exchangeable Sodium Percentage, Exchangeable Sodium Ratio and Sodium Adsorption Ratio: The exchangeable sodium percentage (ESP) is dependent both on the total cation concentration and on the relative proportion of soluble cations. Empirically, U.S. Salinity Laboratory Staff (1954) found that the relationship between soluble and exchangeable cations in salty soils was best expressed by the use of the sodium adsorption ratio (SAR) and the exchangeable sodium ratio (ESR). The SAR refers to the solution phase and is defined as:

$$SAR = \frac{Na^+}{\sqrt{\frac{1}{2} (Ca^{++} + Mg^{++})}} \dots\dots\dots 1$$

all ions expressed as me./l

The ESR refers to the exchangeable cations and is defined as:

$$ESR = \frac{\text{exch. } Na^+ \text{ (me./100 gm)}}{CEC - \text{exch. } Na^+ \text{ (me./100 gm)}} \dots\dots\dots 2$$

The exchangeable sodium can be calculated as the difference between soluble sodium determined in solution and 'soluble plus extractable sodium' using neutral 1M ammonium acetate as an extractant. The ESP can be computed by the following equation:

$$ESP = \frac{\text{exch. } Na^+ \text{ (me./100 gm)}}{CEC \text{ (me./100 gm)}} \times 100 \dots\dots\dots 3$$

The relation between ESP and SAR is given by (U.S. Salinity Laboratory Staff, 1954):

$$ESP = \frac{100 (-0.0126 + 0.01475 SAR)}{1 + (-0.0126 + 0.01475 SAR)} \dots\dots\dots 4$$

This relationship is of importance in diagnosing saline and alkaline soils, since it enables an appraisal of ESP from the values of the soluble cations in saturation extracts.

The ESP, SAR and ESR values were estimated for the Duagh soil and the relationship that these measurements have to one another was determined over the moisture range studied. The results are shown in Table 15 and it would appear that, in general, a decrease in moisture content resulted in increased values of SAR, ESR and ESP. The ESP values calculated from equation 4 are compared with those calculated from equation 3 (Table 15). There appears to be considerable variation between the two sets of data. It was thought desirable to calculate the correlation coefficient and a regression equation for SAR vs ESR values reported in Table 15. The relation thus obtained is shown graphically in Fig. 15. The regression line of U.S. Salinity Laboratory Staff (1954) shown by a dotted line is also included for comparison. The correlation coefficient (r) was +0.856 which is significant at 1 per cent level and is in agreement with the findings of other workers (U.S. Salinity Laboratory Staff, 1954; Banerjee, 1959; Groenewegen, 1961). The regression equation was found to be $Y = 0.0378 + 0.00674 x$, where Y is the ESR and x the SAR. To estimate ESP in the present study, it is expressed in a manner similar to that used by the U.S. Salinity Laboratory Staff (1954). Thus the relationship between the ESP and SAR is given by the equation:

$$ESP = \frac{100 (0.0378 + 0.00674 SAR)}{1 + (0.0378 + 0.00674 SAR)} \dots\dots\dots 5$$

TABLE 15

Sodium Adsorption Ratio (SAR), Exchangeable Sodium Ratio (ESR)
and Exchangeable Sodium Percentage (ESP) for the Duagh Soil
at Various Moisture Contents

Moisture (%)	SAR	ESR	ESP		
	Calc. Eq. 1	Calc. Eq. 2	Calc. Eq. 3	Calc. Eq. 4	Calc. Eq. 5
Ap (0 - 4")					
7.0	37.6	0.15	12.9	35.2	22.6
27.8	26.4	0.13	11.3	27.5	17.8
35.1	25.3	0.12	10.8	26.5	17.2
42.4	24.1	0.12	10.4	25.6	16.7
56.6	22.0	0.11	9.9	23.8	15.7
100	17.7	0.12	10.5	19.9	13.6
Bnt (4 - 15")					
5.2	70.6	0.68	40.4	50.7	33.9
24.0	45.4	0.45	30.9	39.7	25.6
31.0	40.5	0.41	29.0	36.9	23.7
38.1	39.2	0.34	25.4	36.1	23.2
66.2	27.0	0.30	22.9	27.2	18.0
100	20.1	0.29	22.5	22.1	14.8
Csa (15 - 23")					
4.4	95.0	0.56	35.8	58.1	40.4
18.4	66.7	0.41	29.0	49.3	32.8
25.4	51.1	0.42	29.3	42.6	27.7
32.5	48.2	0.35	25.7	41.1	26.6
70.8	29.4	0.22	17.9	29.6	19.1
100	20.5	0.23	18.5	22.5	15.0
C (23" -)					
4.2	88.9	0.63	38.6	56.5	29.5
20.6	59.7	0.53	34.8	46.5	26.0
27.9	51.4	0.42	29.6	42.7	27.8
35.1	39.9	0.43	30.4	36.6	23.5
74.6	31.6	0.21	17.4	31.2	20.1
100	27.9	0.16	14.0	28.5	18.4

The ESP values calculated by equation 5 are shown in the last column of Table 15. A comparison of these values with those obtained by equation 3 revealed that although variations do exist, they are nevertheless less striking than to those obtained by equation 4. Therefore, it would appear that the determination of ESR and SAR relationships at various moisture contents in the Duagh soil resulted in a better estimate of ESP. Levy and Mor (1965) concluded that the SAR and ESR relationship, as suggested by U.S. Salinity Laboratory Staff (1954), can be applied to Israeli soils. However, if this relationship is obtained separately for each soil type, the exchange behaviour of a given soil is more clearly seen. They are of the opinion that for the calculation of ESP better results will be obtained if, for each soil type, its own parameters are used and the present study supports this view. The relationship between SAR and ESP calculated by equation 3 is shown in Fig. 16. A highly significant correlation was obtained ($r = 0.834$) in accordance with the earlier findings reported elsewhere (Lewis and Juve, 1956; Longenecker and Lysterly, 1959).

The experimentally determined ESP is a controversial value and warrants a brief discussion. In extracting soil with ammonium acetate solution it was assumed that this reagent removed the sodium that dissolved in equilibrium solution at a specific moisture content, all the exchangeable sodium, but none of the other more insoluble forms of sodium which may be present in the soil. Several workers (Kelley, 1957; Overstreet and Schulz, 1958; Babcock, 1960) have suggested that soils of arid regions, especially those having high pH values, may contain sodium compounds or

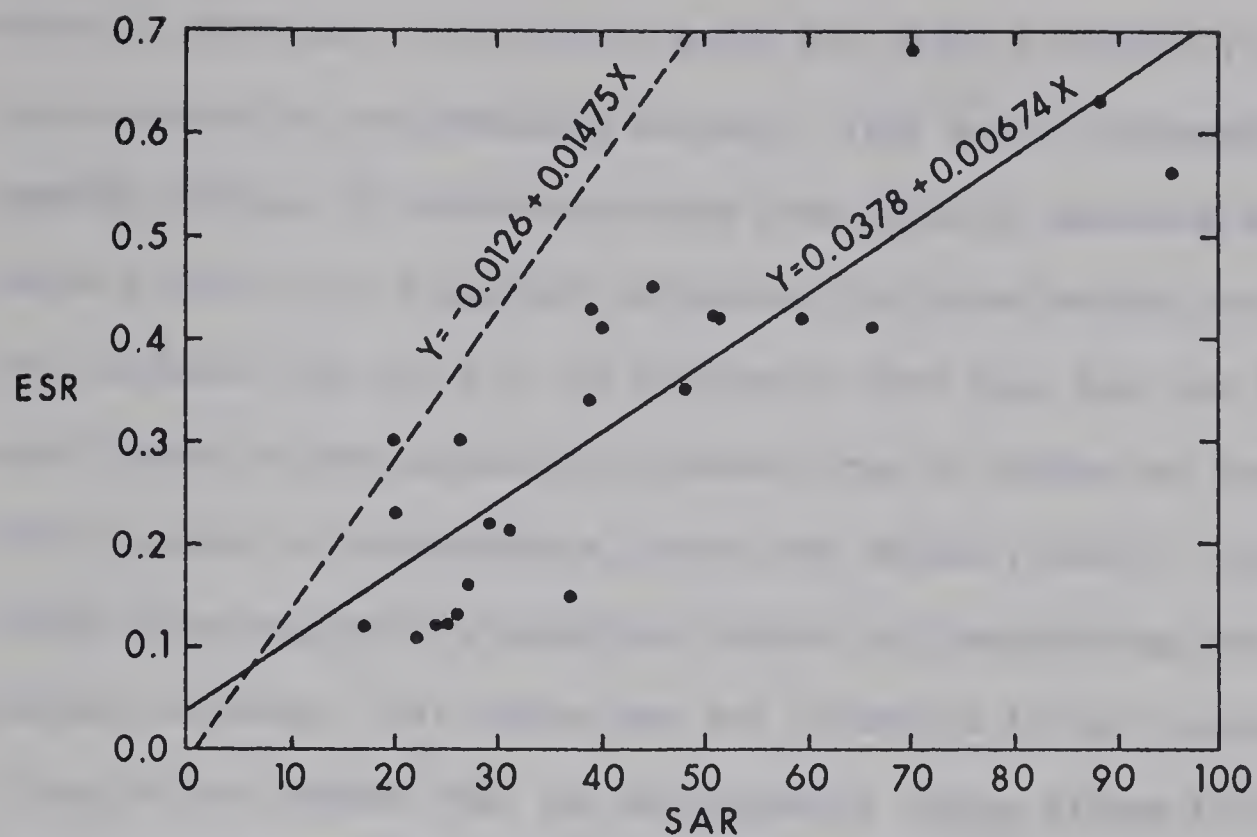


Fig. 15. Relation between SAR and ESR for Duagh silt loam soil

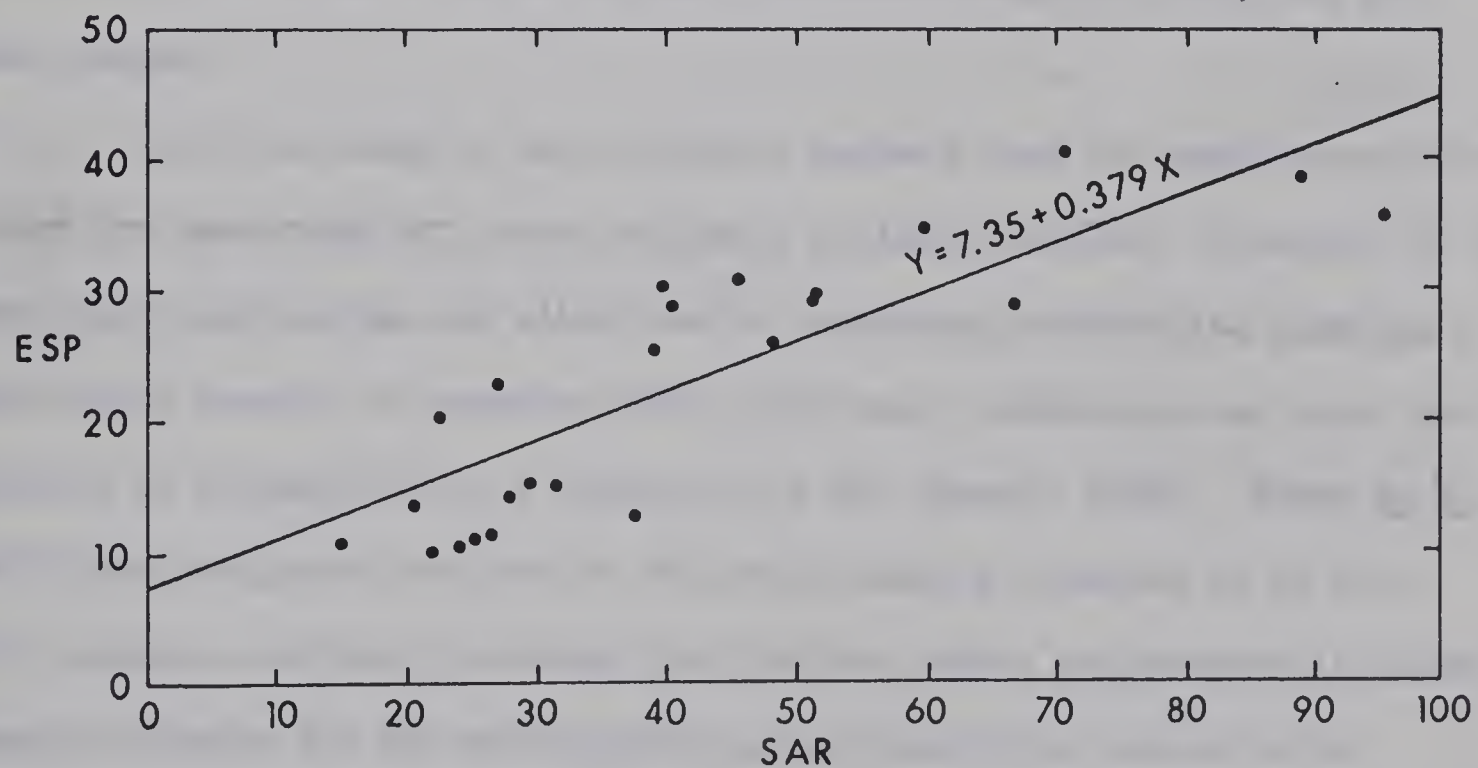


Fig. 16. Relation between SAR and ESP determined by Eq. 3 for Duagh silt loam soil

minerals which are insoluble in water but which dissolve or decompose upon extraction with ammonium acetate. This would, therefore, result in greater amounts of sodium extracted from soils by ammonium acetate. Babcock (1960) has suggested an isotopic dilution method for overcoming this problem, but there is no assurance that Na_{22} does not also equilibrate to some extent with those forms of sodium not readily water-soluble or exchangeable (Bower and Hatcher, 1962). Levy and Mor (1964) have suggested a graphical method for determining such forms of sodium, although, this method was not attempted in the present investigation. It would thus appear that the exchangeable sodium values in this study were obtained without eliminating the possibility of errors due to dissolution of sodium from relatively insoluble compounds that may have been present.

In this study it has also been assumed that the ammonium acetate method for measuring CEC gives uniformly reliable results. However, it is known that some saline and alkali soils containing vermiculite clay fix appreciable amounts of ammonium ions under moist conditions and that this fixation is accompanied by a reduction of CEC (Bower, 1950). Bower et al (1952) have suggested the use of 1N sodium acetate solution of pH 8.2. This procedure although avoiding the fixation errors encountered in using ammonium acetate for CEC measurements gives inaccurate results with soils having a pH value in excess of 8.2, because their content of adsorbed cations is likely to exceed the amount of sodium adsorbed at pH 8.2 (Kelley, 1957). The literature suggests that there is still no agreement on whether to use 1N ammonium acetate solution of pH 7 or 1N sodium acetate

solution of pH 8.2 as a replacing salt. Because of such differences of opinion, the CEC of soil should be specified in terms of pH of replacing solution and the kind of salts employed. In view of the foregoing it would appear that in general the ESP values based on equation 3 are likely not very reliable.

Longenecker and Lyerly (1959) have pointed out that the only reliable criterion of exchangeable sodium in irrigated soils containing salts apparently is to be found in the composition of saturation extracts from these soils. The SAR values can be determined accurately provided methods are available for the measurements of sodium, calcium and magnesium concentrations in soil solutions. The Atomic Adsorption Spectrophotometric technique used in this study for the determination of these cations in equilibrium solutions is generally suitable both in precision and accuracy (Pawluk, 1967). Therefore, it is postulated that, in general, the SAR of equilibrium solutions at various moisture contents would be, perhaps, the best value for determining the exchangeable sodium status of the soils. Bower and Hatcher (1962) have also suggested that ESP values can be estimated most reliably by using SAR values of the saturation extracts. Overstreet and Schulz (1958) found a fair relation between the yield of beans grown on Fresno soil and ESP estimated by SAR. However, the relation between yield and ESP by ammonium acetate extraction was poor.

pH vs ESP, ESR and SAR: The use of pH as a diagnostic tool in alkali soils depends largely on how well the values reflect the exchangeable sodium status of the soil. The hydrolysis of sodium soils tends to be associated with an increase in hydroxyl ion activity; that is pH will be

dependent upon the amount of sodium adsorbed and the degree of hydrolysis prevailing (Kelley, 1951). A number of correlations were obtained to clarify the relation of SAR, ESR and ESP with pH of suspension and filtrate of the Duagh soil when equilibrated at different moisture contents. The correlation coefficients and coefficient of determination values are shown in Table 16. The pH of filtrates and suspensions were highly correlated with ESR and ESP determined by Eqs. 2 and 3 respectively, but less poorly with SAR although significant at 5 per cent level. Furthermore, the data show that the pH of filtrates provide a better correlation with ESP and ESR than those of suspensions. It will be noted that variation in pH of filtrates may explain as much as 65 and 55 per cent of variance in ESP and ESR respectively (Table 16). Fireman and Reeve (1948), U.S. Salinity Laboratory Staff (1954) and Banerjee (1959) are of the opinion that there does not appear to be any useful general relation between ESP and pH values of a soil. They concluded that prediction of ESP values from pH determinations are not feasible. On the other hand, Fireman and Wadleigh (1951) and Agarwal and Yadav (1956) showed that ESP could be predicted from pH values. However, the U.S. Salinity Laboratory Staff (1964) emphasizes the testing of the reliability of this relationship fully before use on any given group of soil samples. However, it is evident from Table 16 that a good relationship exists between ESP and pH (filtrate) for the Duagh soil.

TABLE 16

Statistical Data Pertaining to the Relations of
ESP, ESR and SAR with pH for the Duagh Soil

Comparisons	r	$r^2 \times 100$
ESP vs pH (suspension)	0.673	45
ESP vs pH (filtrate)	0.805	65
ESR vs pH (suspension)	0.651	42
ESR vs pH (filtrate)	0.743	55
SAR vs pH (suspension)	0.489	24
SAR vs pH (filtrate)	0.411	17

$r = 0.404$ at $P = 0.05$

$r = 0.515$ at $P = 0.01$

Effect of Certain Cation Ratios on Plant Growth

Materials and Methods:

Following the equilibrium study described in the previous section, a greenhouse experiment was carried out with the aim of examining the possible effects of $\frac{\text{Na}^+}{\text{K}^+}$ and $\frac{\text{Mg}^{++}}{\text{Ca}^{++}}$ ratios and ionic strength of the solutions on plant growth and nitrogen uptake. It was not practical within the scope of this thesis to attempt to test the effects of all the cation ratios discussed previously. The experiment included 41 different solutions, details of which are described hereafter.

The solution shown in Appendix 1 was used as a base nutrient solution. Different amounts of salts were added to this solution in order to bring ion ratios and concentrations to certain prescribed levels. The concentrations of Na, K, Ca, Mg, HCO_3 and SO_4 in solutions 1_1 , 2_1 , 3_1 and 4_1 correspond to those of equilibrium solutions of the Duagh Ap horizon at saturation, $1/3$, $\frac{1/3 + 15}{2}$ and 15 atm percentage respectively (Table 12). The concentration of sulfate, however, in some cases were slightly different. Solutions 5_1 , 6_1 , 7_1 and 8_1 contained the same amounts of Na, Ca and HCO_3 as in 1_1 , 2_1 , 3_1 and 4_1 respectively but K, Mg and SO_4 concentrations were rather different in order to adjust the molar ratios of $\frac{\text{Na}}{\text{K}}$ and $\frac{\text{Mg}}{\text{Ca}}$ (Table 17) at levels approximately equal to those found in equilibrium solutions of the Malmo surface horizon. This was done by adding calculated amounts of potassium sulfate and magnesium sulfate to the solutions. Solutions 3_3 and 7_3 correspond to 3_1 and 7_1 respectively but contained no ammonium nitrate (Appendix 1). Thus the former solutions contained

only 54.5 per cent as much nitrogen as the latter solutions. Similarly solutions 9_1 , 10_1 , 11_1 and 12_1 correspond to the equilibrium solutions of the Duagh Bnt horizon at saturation, $1/3$, $\frac{1/3 + 15}{2}$ and 15 atm percentage respectively (Table 12). The $\frac{\text{Na}}{\text{K}}$ and $\frac{\text{Mg}}{\text{Ca}}$ ratios were adjusted as described before in the corresponding solutions 13_1 , 14_1 , 15_1 and 16_1 respectively (Table 18) to correspond to those of the Malmo soil. The solutions 11_3 and 15_3 correspond to 11_1 and 15_1 respectively but contained no ammonium nitrate.

A second series of solutions was prepared so that the ionic strengths were approximately equal to those found for the equilibrium solutions of the Malmo soil (Table 13). The $\frac{\text{Na}}{\text{K}}$ and $\frac{\text{Mg}}{\text{Ca}}$ ratios were, however, the same as in the foregoing solutions for the Duagh soil. The concentrations of different constituents added to the base nutrient solution were 20 fold less than present in solutions simulating the Duagh Ap horizon (1_1 to 8_1 , 3_3 and 7_3) in order to get the corresponding dilute solutions 1 to 8, 3_2 to 7_2 respectively. For solutions 9 to 16, 11_2 and 15_2 a 100 fold reduction in concentration was required than present in the corresponding concentrated solution, simulating the Duagh Bnt horizon (solutions 9_1 to 16_1 , 11_3 and 15_3 respectively). The ionic strength of the foregoing solutions was thus reduced approximately to that of the Malmo soil equilibrium solutions at various moisture contents.

For comparison a standard nutrient solution (Appendix 2) was also included in this experiment and the solution is designated by N (Tables 17 and 18). The concentrations of nitrogen, phosphorus and chloride in the base nutrient solution (Appendix 1) were essentially the

TABLE 17

Yields, Nitrogen Content and Root Growth of Barley Grown in Sand Culture Involving Solutions of Different Ionic Strengths and Ion Ratios (Solutions Simulating Duagh Ap Horizon: 1₁ - 4₁ unadjusted; 5₁ - 8₁ adjusted ratios; 3₃ and 7₃ low nitrogen; 5 - 8 and 7₂ diluted solutions)

Solution No.	I moles/l x 10 ³	Na ⁺ K	Mg ⁺⁺ Ca	Yield gm/pot	Stat. sig.**	Nitrogen per cent	Stat. sig.**	Root growth*
N	35	0.13	0.70	1.86	a	2.60	a	++++
1 ₁	74	49.7	1.76	1.93	a	5.23	f g	++++
2 ₁	85	51.1	1.89	1.91	a	5.11	f g	++++
3 ₁	91	51.9	2.02	1.76	a b	5.16	f g	++++
4 ₁	97	53.1	2.16	1.58	b c	5.26	g	++++
5 ₁	149	0.70	1.10	1.37	c	4.74	c d	++++
6 ₁	153	0.90	1.10	1.41	c	4.71	c d	++++
7 ₁	149	1.10	1.10	1.39	c	4.74	c d	++++
8 ₁	148	1.30	1.10	1.47	c	4.81	c d e	++++
3 ₃	89	51.9	2.02	1.57	b c	4.13	b	++++
7 ₃	15	1.10	1.10	0.89	d	4.89	d e f	+++
5	15	0.70	1.10	0.93	d	4.65	c	++++
6	15	0.90	1.10	1.06	d	4.73	c d	++++
7	15	1.10	1.10	0.87	d	5.02	e f g	++++
8	15	1.30	1.10	0.94	d	4.98	d e f	++++
7 ₂	13	1.10	1.10	0.29	e	4.56	c	+++

* Visual Rating: +++++ very vigorous; +++++ vigorous; +++ moderate; ++ poor; + very poor

** Means within a column followed by the same letter are not significantly different at P = 0.05 (Duncan's Multiple Range Test)

TABLE 18

Yields, Nitrogen Content and Root Growth of Barley Grown in Sand Culture Involving Solutions of Different Ionic Strengths and Ion Ratios (Solutions Simulating Duagh Bnt Horizon:
 9₁ - 12₁ unadjusted; 13₁ - 16₁ adjusted ratios; 11₃ and 15₃ low nitrogen;
 13 - 16 and 15₂ diluted solutions)

Solution No.	I moles/l x 10 ³	Na ⁺⁺ K ⁺	Mg ⁺⁺ Ca ⁺⁺	Yield gm/pot	Stat. sig.**	Nitrogen per cent	Stat. sig.**	Root growth
N	35	0.13	0.70	1.86	a	2.60	a	++++
9 ₁	296	193	1.76	0.56	c	5.83	e	+++
10 ₁	420	259	2.35	0.21	d e	6.56	f	++
11 ₁	424	265	2.50	0.18	d e	6.62	f	++
12 ₁	476	270	2.96	0.07	f	6.48	f	+
13 ₁	527	0.70	1.10	0.24	d e	5.57	d e	+
14 ₁	684	0.90	1.10	0.90	e	5.76	e	+
15 ₁	637	1.10	1.10	0.12	e	5.90	e	+
16 ₁	676	1.30	1.10	0.12	e	5.96	e	+
11 ₃	422	265	2.50	0.22	d e	5.97	e	++
15 ₃	634	1.10	1.10	0.11	e	5.99	e	+
13	13	0.70	1.10	1.01	b	5.08	c	+++
14	14	0.90	1.10	0.92	b	4.91	b c	+++
15	14	1.10	1.10	0.87	b	5.29	c d	+++
16	14	1.30	1.10	0.90	b	4.92	b c	+++
15 ₂	12	1.10	1.10	0.27	d	4.52	b	+++

* Visual Rating: +++++ very vigorous; ++++ vigorous; +++ moderate; ++ poor; + very poor

** Means within a column followed by the same letter are not significantly different at P = 0.05
 (Duncan's Multiple Range Test)

same as in standard nutrient solution (Appendix 2).

The barley was grown in a similar apparatus to that described by Leonard (1943). Briefly, it consisted of two chambers connected by a glass tube containing a wick. The upper plastic chamber was filled with washed Ottawa sand (20 - 30 mesh) and the lower glass one contained solution. The solutions were drawn up into the sand through the wick. Gateway barley was seeded, 20 kernels in each assembly and thinned to eight after emergence of the crop. Fluorescent lighting was provided from 6 a.m. to 9 p.m. every day and the temperature was set at 60°F at night and 70° during the day. A randomized block design with four replications was used in this study. The solutions were changed every day throughout the experiment. This was done by discarding the solutions of the lower chambers and pouring a new aliquot (250 ml) on the surface of the sand in the upper chamber. Care was taken not to splash solution on the plants, particularly at the early stages of growth. After 27 days from seeding, the plants were harvested by cutting at the base of the stems. They were dried at 70° C overnight and weights recorded. Roots were removed from the sand, washed and examined.

The oven dry plant material was cut into small pieces and then ground in a Wiley mill to pass through a 20 mesh sieve. Nitrogen determinations were made for each sample, in duplicate, by a modified macro-Kjeldahl method to include nitrate (A.O.A.C., 1955).

Results and Discussion:

The yields and nitrogen contents of top growth and visual observations on roots of barley are reported in Tables 17 and 18. For comparison the yields obtained from the nutrient solution and the nitrogen percentage in plants were taken as standard.

Solutions simulating the Duagh Ap horizon: It will be noted from Table 17 that there were no significant differences in yields from solutions N, 1₁, 2₁ and 3₁ even though the $\frac{\text{Na}}{\text{K}}$, $\frac{\text{Mg}}{\text{Ca}}$ ratios and ionic strengths of the latter three solutions simulating Duagh Ap horizon were greater than that of solution N. The yield from solution 4₁ (Duagh Ap, 15 atm) was significantly lower than N, 1₁ (Duagh Ap, saturation) and 2₁ (Duagh Ap, 1/3 atm) but not different from 3₁ (Duagh Ap, $\frac{1/3 + 15}{2}$ atm). A very vigorous root growth was noted for the plants grown in nutrient solution (N) as compared to the others. It is noteworthy that the nitrogen contents of plants from solutions simulating the Duagh Ap horizon without adjusted ratios (solutions 1₁ - 4₁) were not significantly different, but they were about two fold greater than for plants grown in nutrient solution N (Table 17). During the growing period it was observed that plants from the former solutions were very dark green in colour as compared to those from N. It appears that the high $\frac{\text{Na}}{\text{K}}$, $\frac{\text{Mg}}{\text{Ca}}$ ratios and ionic strength caused a greater uptake of nitrogen from the solutions. In contrast Pálfi (1965) found that the nitrogen levels of rice plants grown in a normal nutrient solution were always higher than that of plants grown on medium rich in sodium. However, it has been found that increased nitrogen supply in the soil as a result of nitrogen fertilization also led

to increased nitrogen uptake by plants grown in a saline soil (Ravikovitch and Porath, 1967; Cairns et al, 1967). It would appear that the plants grown in solutions simulating the Duagh surface soil (solutions $1_1 - 4_1$) utilize the nitrogen effectively. It was found that plants grown in the surface Malmo soil contained more nitrogen when increasing levels of sodium were added equal to those found in the Duagh*. These findings substantiate the results of this study, that is, high $\frac{Na}{K}$ ratios resulted in greater uptake of nitrogen from the solutions having the same nitrogen content. When the amount of nitrogen was reduced in solution, the nitrogen content of the plants was significantly decreased without any appreciable decrease of yield (3_1 vs 3_3).

The yields and nitrogen contents of plants from solutions simulating the Duagh Ap horizon with ratios adjusted (solutions $5_1 - 8_1$) were not significantly different from one another but were reduced significantly as compared to their corresponding unadjusted solutions (solutions $1_1 - 4_1$). It appears that the decrease in yield was caused by higher ionic strength of the solutions. The plants grown in the former solutions were more poorly developed than for the latter. Ravikovitch and Porath (1967) in their experiment also found that increasing salinity generally depressed yield. The data suggest that nitrogen contents of the plants were more affected by ion ratios than by ionic strength. The plants grown in solutions of high $\frac{Na}{K}$ and $\frac{Mg}{Ca}$ ratios, particularly of the former, contained more nitrogen than from solutions of low ratios (solutions $1_1 - 4_1$ vs $5_1 - 8_1$). The nitrogen content of plants from

* Unpublished data, Dr. R. R. Cairns, Canada Department of Agriculture, Vegreville, Alberta.

solution 7₃ was not significantly different from those grown in solution 7₁ even though the nitrogen content of the former was lower; however, the yield was significantly lower for the former.

Plants grown in the diluted solutions with unadjusted ratios (solutions 1 - 4 and 3₂) died before harvest and yields were not recorded. However, the diluted solutions with adjusted ratios (solutions 5 - 8 and 7₂) grew and produced satisfactory root growth but gave significantly lower yields than their concentrated counter parts (solutions 5₁ - 8₁, and 7₃, Table 17). Wiklander (1966) has pointed out that dilution may strongly decrease the uptake of Ca, K and Na by barley plants. This evidently may have some effect on plant yield. Furthermore, it is also realized that the concentration of Ca, Mg, and K in the diluted solutions (solutions 1 - 8, 3₂ and 7₂) were lower than in nutrient solution or in the Malmo soil equilibrium solutions. This may have contributed to the poor growth of plants from these solutions. In contrast Williams (1961) claims that barley plants grow well in dilute culture solutions at potassium concentrations approaching 0.01 ppm. In his experiment the concentration of potassium was adjusted every day to meet the increased feeding ability of the plants. It may be pointed out that the concentrations of potassium in the foregoing diluted solutions was not lower than 2.89 ppm (solution 1). However, Williams (1961) used 100 liters total volume of solution, whereas in this experiment only 250 ml solution was used. Consequently there was much more potassium available in the Williams' (1961) experiment than described here. The nitrogen content of plants from diluted solutions in general, was not significantly different than from their

corresponding concentrated solutions of the same ion ratios (solutions 5 - 8 vs $5_1 - 8_1$). It was noted that germination was delayed from the solutions of higher ionic strength (solutions $1_1 - 8_1$) whilst full germination was obtained from dilute solutions (solutions 1 - 8). However, at the latter stages the subsequent growth of plants was slow from the dilute solutions and plant leaves showed yellowing at the tips.

Solutions simulating the Duagh Bnt horizon: Salt damage was evident in plants grown in solutions simulating the Duagh Bnt horizon with and without adjusted ratios (solutions $9_1 - 16_1$, 11_3 and 15_3 ; Table 18). Germination was greatly retarded and plants were very poorly developed. The yields were significantly lower than from nutrient solution. The root growth of plants was very poor to moderate as compared to very vigorous growth from nutrient solution (Table 18). The data reported in Table 18 substantiate the earlier observations (Table 17), that is, high $\frac{\text{Na}}{\text{K}}$ and $\frac{\text{Mg}}{\text{Ca}}$ ratios were associated with increase in nitrogen content of plants. There was only sparse plant growth from diluted solutions without ratios adjusted (solutions 9 - 12 and 11_2), and the yields were not recorded. However, the plants grew better and root growth was vigorous in diluted solutions when ratios were adjusted (solutions 13 - 16 and 15_2). The yields were significantly greater as compared from their corresponding concentrated solutions (solutions 13 - 16 vs $13_1 - 16_1$).

Ionic strength, ion ratios, yields and nitrogen contents: In general, the data suggest that an increase in ionic strength caused a corresponding decrease in yields. A negative correlation ($r = -0.940$), significant at

one per cent level was obtained between the ionic strength of solutions simulating the Duagh Bnt and Ap horizons with and without ratios adjusted (solutions 1_1 - 16_1) and the yield of barley. Thus it is obvious that about 88 per cent of the decrease in yield may be attributed to the increase in ionic strength of solutions. Ayers et al (1952) have shown that if the saline stress is comparatively high during the early stage, the high salinization later in the growth cycle is either lethal or seriously detrimental to growth and yield of barley. The PK-PNa and PCa-PMg values calculated for solutions 1_1 - 16_1 were significantly correlated with per cent of nitrogen in plants grown in these solutions. The correlation coefficient being 0.544 and 0.539 respectively were significant at five per cent level. However, no significant correlation was obtained between the above IR_o values and plant yields.

Field trials at Vegreville supported by the laboratory and greenhouse findings provide conclusive evidence that the solonetzic soils are incapable of supplying a satisfactory quantity of nitrogen for plant growth (Cairns et al, 1962; 1967). The application of nitrogen on this soil considerably increased the yield and nitrogen uptake (Cairns et al, 1967). In view of the results obtained in the greenhouse experiment described here, it is postulated that the large $\frac{Na}{K}$ and $\frac{Mg}{Ca}$ ratios in equilibrium solutions of the Duagh soil, particularly the former, resulted in a considerably greater uptake of nitrogen. Consequently under the field conditions plants will effectively use nitrogen but its supply may become limited due to the low reserve and thus growth may be impaired. In addition, the high ionic strength of equilibrium solutions

will also exert a deleterious effect on crop yield. Obviously the situation will be further aggravated by increasing depth of root penetration into the lower horizons.

Chapter 5

SUMMARY AND CONCLUSIONS

The productivities of saline and alkali soils, widely spread over the world, have been reduced considerably due to the presence of excess soluble salts. Sodium sulfate has been recognized as the dominant soluble salt present in the solonetzic soils of Western Canada. The success or failure of soil solution analysis, as an aid to plant nutrition guidance or any other use, depends largely on the availability of reliable and accurate analytical procedures. Substantial evidence indicates that the accurate determination of water soluble sulfate in soils always has posed a difficult problem to soil scientists. The accumulation and distribution of ions in the soils due to the upward movement of ground water have also received considerable attention. However, information on the sulfate distribution in solonetzic soils as influenced by the presence of ground water table is rather meager. Finally, the present knowledge with regard to ion ratios in equilibrium solutions of solonetzic soils in the field moisture range is very limited. It could be postulated that the effect of these ratios is related to the productivity of these soils.

The present investigation was designed with the following objectives: (i) to develop an accurate method for determining water extractable sulfate in soils, (ii) to study the sulfate distribution throughout the profile of a solonetzic soil resulting from the presence of water table, and (iii) to determine the true equilibrium solutions in

soils adjusted to different moisture contents and to study various cation ratios in equilibrium solutions and other properties of a solonchic and a chernozemic soil. An attempt was made also to determine the effect of some cation ratios on yield and nitrogen content of barley.

An electrometric method was developed for determining water extractable sulfate in soils. The technique is based on precipitating sulfate in soil extracts with lead and determining the excess of lead ions polarographically. Different soils including a solonchik, a chernozem, a grey wooded and a podzol were used in this study. For soils low in organic matter the method is accurate and satisfactory. However, large amounts of organic matter in soil extracts interfered because the sulfate was held by the organic matter. Furthermore, organic sulfur may be present in water extracts of soils high in organic matter and this too poses a problem. Other ions normally found in soil water extracts will not interfere. However, this technique will have a limitation if the concentration of chloride ions in soil water extracts is exceptionally high ($>56,4 \text{ mmol/l}$). The method is simple and accurate for determining water extractable sulfate in most soils.

Sulfate movement in Thin Duagh loam soil as influenced by the presence of a water table was studied and details of the technique used are described. Soil columns containing different horizons were used and the movement of sulfate was followed with the use of S^{35} tagged sodium sulfate. The concentration pattern showed that retention was greater in the surface soil, relatively high in organic matter, than at lower depths. The data support earlier findings that sulfate tends to move

more slowly than water in soil. The sulfate distribution in the profile did not appear to have any consistent relationship with pH, acid soluble phosphorus and clay content of the soil horizons.

A study was initiated to achieve objective (iii) which, in fact, was the central theme of the present investigation. Two profiles, a Black Solonetz (Duagh silt loam) and an Eluviated Black Chernozem (Malmo silt loam) were sampled and characterized chemically. For the determination of gypsum in the soils, an X-ray technique was used. The chemical characteristics of the Duagh soil clearly distinguish it from the Malmo. There was an abundance of soluble salts in the Duagh soil, the dominant being sodium sulfate. There was essentially no gypsum present in the Malmo soil, but the sub-surface horizons of the Duagh contained appreciable amounts. Per cent organic matter and nitrogen were greater in the Malmo soil than in the Duagh.

Results of the preliminary greenhouse experiment clearly demonstrated the detrimental effects of increasing sodium levels in soils on the barley yield. Better yields were obtained from gamma irradiated soils when no sodium sulfate was added. The data also indicated that nitrogen applied as ammonium sulfate was significantly more effective in increasing barley yield than that applied as sodium nitrate.

A method is described for determining the true equilibrium solutions for Duagh and Malmo soils, adjusted to various moisture contents, by interpolation of ion concentrations in solution before and after equilibration. The data provide evidence that the equilibrium between solid and solution was achieved by a one-hour shaking period. The

technique permits the determination of composition and ion ratios in true equilibrium soil solutions for soils at various moisture contents normally encountered under the field conditions. The increase in moisture resulted in a corresponding decrease in concentration (mmol/l) of various constituents in equilibrium solutions of both soils. The only exception being for the calcium concentration in the sub-surface horizons of the Duagh soil. Due to dissolution of solid gypsum present, the calcium concentration was increased with increasing moisture. It does not appear feasible to calculate the solubility of gypsum in equilibrium solutions at various moisture contents by the solubility principle alone. It is postulated that in equilibrium solutions of high ionic strengths sulfate ions will be associated with cations to form undissociated ion-pairs.

The ionic strengths of equilibrium solutions of the Duagh soil were considerably greater than for the Malmo soil. For the former soil the values were considered to be too high for the calculation of activity coefficients; therefore, concentration ratios were used. However, for the Malmo the ratios were expressed in terms of activity. The changes in ratios for the ion-pairs $K-(Ca + Mg)$, $K-Na$, $Ca-Na$, $Mg-Na$, and $Na-(Ca + Mg)$ with variation in moisture content in the different horizons of the two soils studied are discussed. The results are explained on the basis of cation exchange, dilution effect and dissolution of solid salts present. Over the moisture range studied the IR_o values for various ion-pairs for the Duagh soil were markedly different as compared to the Malmo. It was postulated that soil and solid salts were in equilibrium with solutions over the low moisture range in the sub-surface horizons of the Duagh soil.

Thus the variation in moisture resulted in a marked change in ionic strength and IR_o values over this range. However, in the surface Ap of the Duagh and in all the horizons of the Malmo soil changes in moisture caused only a gradual change in these values.

Schofield's 'Ratio Law' was confirmed and the equilibrium remained relatively undisturbed over the moisture range studied for most of the ion-pairs in the Malmo and the surface Duagh soil. However, for the sub-surface horizons of the latter soil the data were not consistent with the Law and equilibrium position was changed at every moisture content studied. This was attributed to the presence of excess salts in the soil.

Sulfate was the principal anion present in the equilibrium solutions of the Duagh soil. The variation in sulfate concentrations had a significant effect on IR_o values for various ion-pairs. The effect was more marked on PK-PNa as compared to other ratios. It was postulated that the upward movement of sulfate due to the presence of a ground water table and its distribution in the Duagh profile may have an important bearing on the plant growth by changing the IR_o values.

For both soils the electrical conductivities of the equilibrium solutions increased with decrease in moisture and were significantly correlated with ionic strengths. In the field moisture range the osmotic pressures of equilibrium solutions of the Duagh sub-surface horizons were regarded as being too high for normal growth of plants. In general, decrease of moisture in the Duagh soil resulted in increased values of sodium adsorption ratios (SAR), exchangeable sodium percentages (ESP) and exchangeable sodium ratios (ESR). The SAR of the equilibrium solutions

at various moisture contents was found to be a significantly reliable index of ESP. The following equation was established for deriving ESP values for the Duagh soil.

$$ESP = \frac{100 (0.0378 + 0.00674 \text{ SAR})}{1 + (0.0378 + 0.00674 \text{ SAR})}$$

The data suggest that the pH of the equilibrium solutions provided a better estimate of ESR and ESP than those of the corresponding suspensions.

A greenhouse experiment in sand culture was conducted with the aim of examining the possible effects of $\frac{Na}{K}$, $\frac{Mg}{Ca}$ ratios and ionic strength of solutions on the yield and nitrogen contents of barley. A number of solutions were used which consisted of ion ratios and ionic strengths corresponding to those found over the field moisture range in the Duagh Ap and Bnt horizons and also approximately equal to those found in equilibrium solutions of the Malmo soil. The high ionic strengths of solutions simulating Duagh soil caused a considerable delay in germination and yields were depressed. A negative significant correlation was obtained between the ionic strength of solutions and barley yield. The high $\frac{Na}{K}$ and $\frac{Mg}{Ca}$ ratios in solutions, particularly the former, increased considerably the nitrogen content of the plants. The PK-PNa and PCa-PMg of solutions were significantly correlated with nitrogen content of plants whilst no correlation existed with yield. The growth was greatly depressed and plants died at the latter stage of growth for the dilute solutions of ionic strengths approximately equal to those of equilibrium solutions of the Malmo soil while the ion ratios were the same as found for the Duagh

Ap and Bnt horizons. Apparently the concentration of K, Ca and Mg were too low, particularly of K, for the normal growth of plants. A better yield was obtained from diluted solutions of ion ratios and ionic strengths approximately equal to those found in Malmo soil. The concentration of potassium in these solutions was appreciable as potassium sulfate was added to adjust ion ratios and it is reasoned that this was largely responsible for the improved growth.

In general, the results of this greenhouse experiment further illustrate the importance of nitrogen as related to the productivity of the Duagh soil. The high negative correlation between ionic strength and yield and the effect of increasing $\frac{\text{Na}}{\text{K}}$ ratios on increased nitrogen uptake were also of considerable interest.

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Appendix I

Base Nutrient Solution Used in the Greenhouse Experiment

	gm/l
NH_4Cl	0.0916
$\text{NH}_4\text{H}_2\text{PO}_4$	0.4227
NH_4NO_3	0.1800
Ferric citrate	0.0200
H_3BO_3	0.0005
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	0.00154
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.00088
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.00025
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.00001
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.00002

Appendix 2

Nutrient Solution (Hewitt, 1952)

	gm/ l
KNO_3	1.000
KH_2PO_4	0.5000
NaCl	0.1000
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.5000
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.5000
Ferric citrate	0.0200
H_3BO_3	0.0005
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	0.00154
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.00088
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.00025
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.00001
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.00002

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